Florida Agricultural
Experiment Station Library
Gainesville, Florida



Digitized by the Internet Archive
in 2013

http://archive.org/details/caseinitsuses00hade

CASEIN AND ITS USES

CHEMISTRY MANUFACTURE AND COMMERCIAL APPLICATIONS OF CASEIN INCLUDING FORMULAE AND RECIPES.

By

HANS HADERT

Translation of Second German Edition
with Additions

By

DR. HENRY GOLDSMITH



1938

CHEMICAL PUBLISHING COMPANY OF NEW YORK
NEW YORK, N. Y., U. S. A.

388
H128c
AGRI-
CULTURAL
LIBRARY

Copyrighted 1938

By

Chemical Publishing Company of New York, Inc.

PREFACE

In 1934 I published a booklet with the same title as this one, representing a special copy of some of my articles in the journal "Gelatine, Leim, Klebstoffe". Although it has been out of print for some time, the requests for it have not diminished.

The second edition, now appearing, is completely new in form and very considerably enlarged. I have emphased particularly the chemistry and the manufacture of the casein, since so much difference in opinion exists about this among producers of casein products. Formulas successful for a long time were found unsuitable because another type of casein was used, and new experiments became necessary. I have tried to explain by many examples and formulas the differences of the caseins, and the possibilities of influencing their properties. A collection of formulas was added to the chapters on casein glues and on casein paints and paint binders which was enlarged considerably, in comparision to the first edition. I shall be glad if this edition meets with as much acclaim as the first one and, with this hope, I turn over this book to the public.

Berlin-Frohnau

Hans Hadert

18534

TRANSLATORS NOTE

Because of the need for a modern book on the technology of casein and its applications, I feel that this book will be most welcome and helpful to technicians and industrial users of casein. The author is a recognized expert in the field of casein adhesives.

The translation has been made in a manner that best carries out the ideas of the author. Additional formulae have been included in the last chapter to better show the varied uses to which casein is put in modern industry.

Dr. Henry Goldsmith

C O N T E N T S

	PAGE
CHAPTER I	1
Chemistry and Manufacture of Casein	
CHAPTER II	27
Casein Adhesives	
CHAPTER III	60
Casein Paints and Colors	
CHAPTER IV	82
Other Applications of Casein	

CHAPTER I

CHEMISTRY AND MANUFACTURE OF CASEIN

Of all the proteins, casein seems to find the widest technical application, although it belongs to those organic compounds which are most difficult to investigate. It is a complex protein, and the complex phosphoproteins particularly offer the greatest difficulties to investigation.

It has been shown over and over again, that casein is not the simple substance for which it has always been taken. Even today, the opinions of serious scientists differ on the classification of the casein (lipoids or proteins.)

Casein which will essentially be treated in this book, together with some less important proteins, is found primarily in the milk of mammals. Even here it can be observed that it is not present in the same form in the various cases, depending on the different composition of the milk, the age of the cow, the feed given, and even upon the time of the milking. If calving is to occur or has taken place, this will also have an influence on the milk and therefore also on the composition of the casein.

Whereas formerly (and even today in some smaller countries) casein was obtained in very irregular composition by simply acidifying skim milk and thus precipitating the casein, science has today invaded the field of casein production. It has, for instance, been found, that the most favorable pH for the acidification is 4.6. This was not only found in the laboratory, but proved by many years of practice.

The average composition of cow milk, according to Prof. Dr. O. Gerngross, is the following:

	Normal Whole Milk %	Primary Milk (Colostrum) %
Water	87.6	78.7
Casein	3.15	4.
Albumen	0.35	5
Globulin	Traces	5.3
Milk Fat	3.4	4.
Lactose	4.6	1.5
Citric Acid	0.14	-
Extractable Matter	0.01	-
Ash	0.75	1.

In the primary milk mentioned, we deal with the first milk of a cow immediately after calving. Such milk is unfit for the production of casein, because of the high content of albumen and globulin, which would cause trouble.

In the major countries of casein production, and recently in a very large measure also in Germany, skim milk is used for the production of casein. From this milk, the casein or the curd is obtained by acidifying with various acids, including hydrochloric acid, sulphuric acid, and lactic acid (the latter either by natural self-souring or by addition of an acid whey.) The curd forms by warming the milk up to 34-35°C. and by adding hydrochloric acid until a pH value of 4.6-4.8 has been reached. It is then allowed to settle and is freed of the whey by pressing it through curd presses. The curd is then repeatedly washed with dilute hydrochloric acid (without being allowed to dry out) in order to remove all impurities. The curd thus treated is then dried and yields a casein which is suitable for most technical purposes. Repeated washing and pressing is necessary to obtain particularly pure grades. In this case, ammonia may be added, and filter presses may be employed to remove the water. In large-scale manufacture, centrifuges are used for this purpose. It must always be borne in mind that the hydrochloric acid used should not have a pH higher than 4.8.

The best method of casein production is that described in the Studies on Casein by Linderstroem and Lang, which is as follows:

20 liters of fresh and unpasteurized skim milk are precipitated at room temperature (20°C.) with about fifteen liters of 0.05 N hydrochloric acid. The acid is added with

thorough agitation in portions of 0.5 liters. After each addition, the milk is allowed to stand for five to ten minutes. When, by its appearance, the suspension indicates that an optimum of precipitation is approached, it is kept stirring for two hours. Thereafter, the balance of the acid is added in small portions of about ten to fifty cc. The precipated casein is filtered off through cloth and is washed five times with 30 liters of distilled water each time. During the last washings, the filtrate comes through cloudy and contains emulsified fat together with a very fine casein suspension. The last wash liquor is pressed off, as well as possible, and to the precipitate with its adhering moisture (7 liters), an equal volume of ninety-six percent alcohol is added. The mixture is left standing for half an hour with stirring. After filtering, 10 more liters of 96% alcohol are added to the precipitate and after three additional hours of stirring it is filtered again and the casein is mixed with 10 liters of absolute alcohol. The mixture which remains standing until the next day, is then filtered and the precipitate is treated three times with 10 liters of ether each time. The casein is dried first in the air and finally for 24 hours in vacuo, over sulphuric acid. The yield from 20 liters of milk is 545 grams of casein of chemically pure quality. It is a white powder and is very hygroscopic.

For the production of technical casein the process is simpler and requires less caution. Particularly the many washings are dispensed with. The removal of the fat, which is necessary in large-scale production of casein from whole milk, is not left only to the dairies. These remove the fat of the milk in centrifugals down to a content of 0.05-0.2%. The skim milk is therefore further freed from fat so that the casein produced from it does not contain too much fat which is detrimental.

The skim milk, when received in the casein factories, is therefore at first neutralized with sodium bicarbonate or sodium carbonate and centrifuged anew. It is acidified therefore; the curd thus formed is washed and its moisture is reduced to 55% by pressing it in curd presses. The drying should not be carried too far, and should be done in vacuo if possible. The curd thus obtained consists on the average of 70 to 75% of water, 20 to 25% of casein and small proportions of fat, lactose, and lactic acid. The production of casein may be summarized by the following flow-sheet:

1. Casein Production by Self-Souring

Arrival of fresh skim milk from the separator

↓

Let stand at 27-32°C. until it coagulates

Heat to 46-54°C. with ejector — Heat to 43-53°C. in a vessel

Grainy curd, easily washed — Acid whey For feeding purposes — Lumpy curd, hard to wash

Wash, press, grind, dry — Wash, press, grind, dry

Lactic acid - ejector casein, low ash content and viscosity

Lactic acid - casein, medium ash content and viscosity

2. Casein Production with Hydrochloric Acid at 34-36°C.

Arrival of fresh skim milk from the separator

↓

Heat to 34-36°C. with 1.10 liters of hydrochloric acid to each thousand liters of skim milk.

Whey for lactose production — Grainy curd, easily washed

Wash, press, grind, dry

↓

Fine-grain casein, low ash content and viscosity

3. Casein Production with Hydrochloric Acid at 46-49°C.

Arrival of fresh skim milk from the separator

Heat to 46-49°C. with 0.5 liters of hydrochloric acid to each thousand liters of skim milk.

- Whey for lactose production
- Lumpy curd hard to wash
 - Wash, press, grind and dry → Hydrochloric acid - press - casein, low ash content and viscosity
 - Heat to 85°C., drain, grind and dry → Hydrochloric acid-heat-casein, high ash content, very high viscosity

4. Casein Production with Sulphuric Acid at 49 to 52°C.

Arrival of fresh skim milk from the separator

Heat to 49-52°C. with 0.25 liters of sulphuric acid for each thousand liters of skim milk.

- Lumpy curd, hard to wash
 - Wash, press, grind and dry → Sulphuric acid-press-casein, high ash content and viscosity
 - Heat to 82°C., Drain, grind, dry → Sulphuric acid-heat-casein, ash content and viscosity high
- Whey, runs off

5. Casein Production with Rennet at 35-36°C

Arrival of fresh skim milk from the separator

↓

Precipitate at 35-36°C. with rennet

↓

Heat to about 60°C.

↓

Fine curd, easily washed — Whey for lactose production and for feeding purposes

↓

Wash, press, grind, dry

↓

Rennet casein, high ash content and viscosity

The sulphuric acid (sp.gr.1.83) is diluted 1:4 with water before precipitation. However, hydrochloric acid is preferred, since it gives a better casein than sulphuric acid, on account of the better solubility of its potassium salt and of its lower ash content.

Basic requirements to get a good casein are the following properties:

1. Very faint or no odor.

2. Smallest possible fat content.

3. Good solubility, clear solutions with alkalies. The drying temperature is of very great influence upon this as the following data show:

Drying temp. of Casein, °C.	Time of Solution in 15% Borax Solution	Type of Solution
85-90	More than 20 minutes	rather thin
96	40 minutes	thick
100	40 minutes	thick
110	40 minutes	thicker than at 100°C.
120	more than 40 minutes	very thick
130	swells but does not dissolve	partial precipitation
140	swells but does not dissolve	slight precipitation
150	slight swelling, insoluble	no precipitation

4. Alkali-soluble with a minimum of foam formation.

5. Definite ash content of the casein. This influences the ability of the casein to absorb water and its viscosity in solutions. The amount of water taken up by the casein to give a solution of a certain viscosity increases (within limits) in proportion with its ash content.

It should be noted in connection with (5.), that those caseins made by using hydrochloric acid or sulphuric acid usually have a high ash content and therefore give highly viscous solutions even with small amounts of casein. Since the viscosity of casein can be influenced as desired by adding more or less acid, or by using higher or lower temperatures, a standardized production of casein requires a precise and continuous supervision, and not an uncontrolled operation. Although it is possible to afterwards influence a casein of a certain viscosity, the methods which can be used for this are only makeshifts. A very viscous casein, for instance, can be transformed into a casein of low viscosity by the addition of 2% of hydrofluoric acid.

It should also be remembered that the highly viscous caseins made with hydrochloric or sulphuric acids are much harder to dissolve than caseins of low viscosity. According to American determinations (Jol. Ind. Engineering Chem. vol. 22, 1930, page 54), caseins give the following results according to the amount of hydrochloric acid used:

Influence of the Amount of Acid Upon Ash Content and Viscosity

Hydrochloric acid, in cc	Ash	Viscosity
1.8	3.86	1020
2.7	3.50	900
3.6	2.79	185
4.5	2.48	130
5.4	2.36	80
6.3	1.97	90

Besides the casein made with acids which is the only one suitable for the production of casein adhesives and casein paint binders, there is also another casein, rennet casein. For the production of this casein, rennet from calf's stomach is used as a precipitant.

The ash content of such a rennet casein is about three times as high as that of an acid casein, its solubility in alkalies is different. It differs from acid casein also in other respects. It is almost odorless when moistened, it is transparent and clear. It is easy to find out whether one is dealing with a rennet casein or an acid casein, by heating a sample of the casein in a test tube to 100-150°C. While rennet casein always remains white under this treatment, acid casein turns brown quickly. Solutions of rennet casein in diluted sodium hydroxide solution keep their pale color, whereas acid casein turns brown the same day when thus treated.

Casein sold under the name of Paracasein is rennet casein.

Rennet casein is used mainly for the production of casein synthetic resins, such as Galalith, by reaction with formaldehyde by which it is made insoluble.

Compositions of various caseins, according to different investigators, are as follows:

% Compositions of Cow Milk Caseins

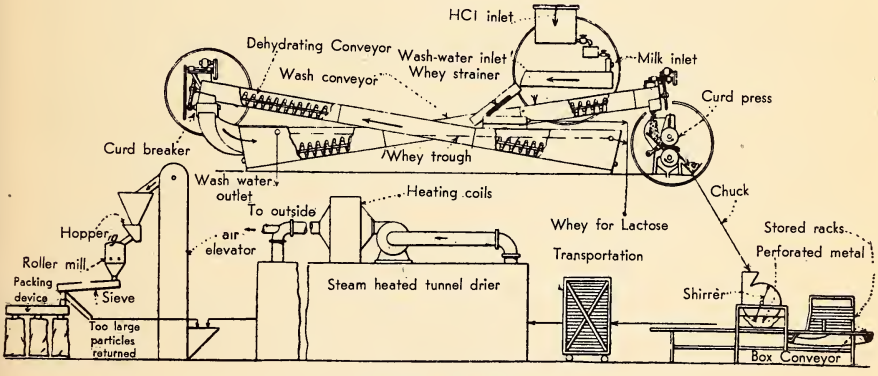
	Hamarsten	Lehmann	Slyke and Bosworth
Carbon	52.96	54.00	53.50
Hydrogen	7.05	7.04	7.13
Nitrogen	15.65	15.60	15.80
Sulphur	0.75	0.77	0.72
Phosphorus	0.85	0.85	0.71

These data show that the composition of the various caseins does not differ very much. However the various grades show considerable differences in their properties when used. The conclusion has therefore been drawn that there are numerous other causes for the different properties besides the variation of the ash content. It is likely

that casein consists of various proteins which all have different properties. It has not been yet possible to penetrate these secrets of nature, but it seems that the calcium complex exerts a very essential influence. According to investigations of Porcher, casein is present in milk in a colloidal solution as a calcium caseinate-calcium phosphate complex. If acid casein is made with hydrochloric acid, the pure and insoluble casein is precipitated out. The rennet precipitation however yields the calcium caseinate as rennet casein.

Let us now consider casein production itself. I shall describe in the following a very modern casein factory of an American firm which has an hourly consumption of 11,500 liters of skimmed-milk and yields 2.65-2.75% casein, in comparision to a yield of 2.25 to 2.40% of other and differently working batch processes.

The working scheme of the plant can be seen from the sketch on this page.



Casein Plant (Sheffield)

Skim milk is heated continuously to 43°C. under thermostatic control in a hot-water heated tubular heat-exchanger. 20°Bé hydrochloric acid is drawn from a rubber-lined storage tank, diluted, and pumped into a stoneware kettle of 475 liters capacity. From this it flows (in amounts which are controlled by titration) through a vessel controlled by a

float valve and a porcelain stopcock, into a small earthenware cylinder containing paddles and serving as a mixer. Here the acid is introduced into a thin jet of hot whey and is mixed in immediately and precipitates out the bulk of the casein curd. To give the reaction time to go to completion, curd, whey, and unchanged whey and acid flow through a stoneware mixing container, from which it empties out through a strainer into a dehydrating conveyor. A considerable part of the whey goes through the strainer and is drawn off together with the whey from the dehydrating conveyor. It is used for the production of feed or for the recovery of lactose or lactic acid.

The dehydrating and the washing conveyors are of like construction and are steel screw conveyors inclined at an angle of 9°. The lowest trough for each conveyor is built in such a way that its uppermost edge is parallel to the level of the liquid. Whey and curd arrive in the first conveyor a little above the center. The whey reaches the outlet by gravity, while the curd is removed to the top by the transport device; there the curd runs over continuously, the flow being interrupted at certain intervals. After some time it reaches the outlet into the curd breaker at the highest point of the dehydrating conveyor. During this process the curd has lost as much of the whey as can be removed by dehydration. The casein arrives at the curd breaker and is there broken up further. It is pressed through a perforated plate by means of a rotating stirrer. Thus the material is prepared for the following thorough washing by counter-current. The curd slides down a chute and is taken up by the washing conveyor which removes it slowly towards the top through a current of cold washing water. After some time, the material has been moved to the upper part of the washing conveyor. The ash content of this material is down to about 1% (the ash content of the casein is determined by a muffle furnace) and the free acidity is lowered to a fraction.

Formerly, the pressing of the casein was a process with great waste of time and work. It necessitated putting the curd into cloths, to press it in hydraulic or mechanical presses, and breaking up the press-cake afterwards. It was found that the moisture content depends very much upon the type of pressing, and that by passing the casein through a three-roller-mill, only the first two rollers do the main work. Therefore, a two-roller-press was constructed for the removal of the water. The water content of the curd will

always be about 54%, no matter which method of pressing has been used. Such a two-roller-press can be seen distinctly on the right side of the sketch. The upper solid cylinder is chromium plated and presses the curd against the lower perforated bronze cylinder by means of a spring. Both cylinders are moved by a motor at a regulated speed, in order to synchronize with the feeding from the screw conveyor. A swinging disk worked by means of an eccentric serves a double purpose. It serves as a hopper as well as to push the curd between the cylinders. The curd is now free of the bulk of the washing water and is cut off from the lower cylinder by means of a wooden knife edge and carried over to the next step of the process. Another machine serves to fill the drying racks, which otherwise requires a large amount of work. The racks consist of wooden frames with wire net bottoms. These are piled up, one on top of the other, at one end of the machine and are pulled through at the same time by a conveyor underneath a distributing cylinder with a perforated metal bottom. A stirring gear inside the cylinder breaks up the curd further and presses it through the perforations into the racks. The filled racks are then loaded on cars and these are moved into a drying tunnel in which the casein is dried for 3 to 4 hours at a temperature of 71-93°C. The curd thus produced contains little acid and will resist a temperature of 93°C. without discoloration. This shortens the drying time to about one half. No action of bacteria is observed during such quick drying. Furthermore, such casein can be stored for at least 50% longer than other caseins of higher acidity without discoloring or losing its adhesive power. Although the drying is not a troublesome process, it still remains necessary to control it thoroughly, first because of the possible damage done by overheating and secondly because of the tendency of the casein to dry on the surface and to form a hard outer skin. According to the U. S. Patent No. 1,892,233, the casein particles are dried by exposing them to a current of air which is controlled in its temperature and humidity. This way, thoroughly dried caseins are obtained in unchanged form.

The racks are moved from the drier and emptied into a bucket conveyor. The material is thus carried to a roller mill, where it is broken up until it passes through a 20-mesh screen. A swinging screen separates the coarse particles, which are ground once again, or passes the product into a bag-filler from which it is filled into triple paper bags holding 34kg. In the procedure described above, one man per shift can control the entire plant from the precip-

itation to the drying. Three other men do all the remaining work.

As the table, given above, on the influence of the drying of the casein on its properties shows, special importance must be given to the drying which is almost more important than the precipitation of the curd itself. In various German and also in foreign casein factories the drying of the casein is done with good success drying through hot air introduced from below. Such a hot air drier is shown by the following reproduction:

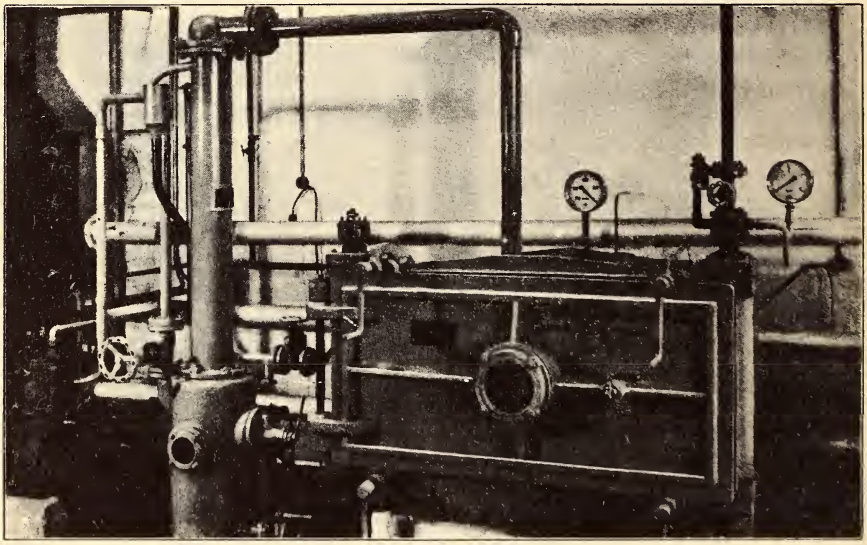


Hot Air Drier for Casein. Hourly output 150kg.
(Seiffert System)

The drier consists of a vessel for the material to be dried. The vessel's bottom consists of wire cloth. Through this wire-bottom, heated air is introduced. The air is pressed into an air chamber through an air-heater by means of a fan. The ceiling of the air chamber is the permeable bottom of the drying chamber. A built-in stirrer scrapes slowly over the permeable bottom and closes the cracks which form in the moist drying material. The hot air penetrates and surrounds the drying matter which is put up in a layer about 250mm high and becomes saturated with humidity and leaves the drier at the top. With progressive drying the material breaks up in many small particles of the size of groats or peas. These small particles are surrounded by hot air from all sides and therefore dry very homogeneously. This is impossible if the casein is stored on racks without being disturbed. The temperature of the air can be regulated at all steps. At the beginning it is favorable to dry at 60-65°C. With continued drying, the temperature is lowered to 30-35°C. and is finally adjusted to room temperature to cool down the material. The drying time itself is $2\frac{1}{2}$ hours, but including the time for filling and emptying of the drier it takes 3 hours. The discharge is automatic by the action of the stirrer which removes the material through a discharge door into a receiver by means of a chute. The amount of heat used is very favorable because of the thorough penetration and good distribution of the drying material in the hot air. Practice shows only 178 to 180kg of steam are needed for 100kg of water evaporated from the material. These driers are in use in different sizes, namely from 30 to 150kg hourly curd output, and are charged with 90 to 450kg of curd for each drying period of three hours. This drying period of three hours per charge is based upon a water content of 65% of the curd. The drier the curd used, the less is the time and the amount of heat needed for the drying. Since about 80kg of curd of 85% water content or 33kg of casein of 10% water content are obtained from 1000kg of skim milk, the driers, if filled three times a day, are sufficient for a daily output of at least 3400 to 16500 liters of skim milk or for a production of 110-540kg of casein a day.

If a vacuum oven is used for the drying of the curd, as is shown on the following page, the pressed curd is filled into drying pans of aluminum which are placed between the heating plates of the vacuum drier. The vacuum drier is closed thereafter, steam is passed through the heating plates and the vacuum pump is started. The vacuum and the heating cause the water of the casein to evaporate very quickly and

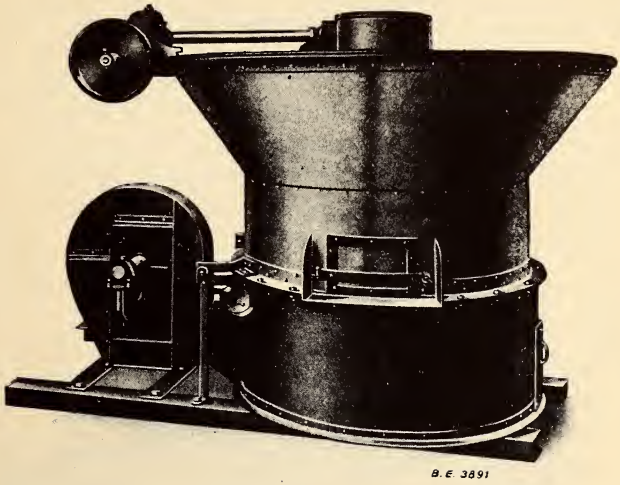
the drying takes place at a low temperature (about 25-40°C.). In the beginning, the bulk of the moisture evaporates and towards the end of the drying hot water is used to replace the steam in the heating plates of the oven. The moisture removed from the casein is removed from the vacuum oven by means of an air pump and is condensed in a surface condenser. It can be observed through windows in the drying oven as well as on the surface condenser and also by various instruments and devices, when all the moisture is removed and the drying of the casein is finished. The vacuum oven is opened thereafter, and the pans with the dried casein are taken out and are replaced by freshly loaded ones.



Small Casein Vacuum Drying Oven (Passburg-Block System)

Another casein drier is shown on the following page. This machine is suitable only for the drying of acid casein. In this drier the casein is put into a funnel shaped tub after being broken up. It is dried there in a current of heated air produced by a fan. The construction of the machine is very simple. It consists of a fan, a heating battery, an air compressor, a drying chamber, a rotating stirrer, a filter disk (to clean the drying air of dust and other impurities) and two perforated metal sheets which are to carry

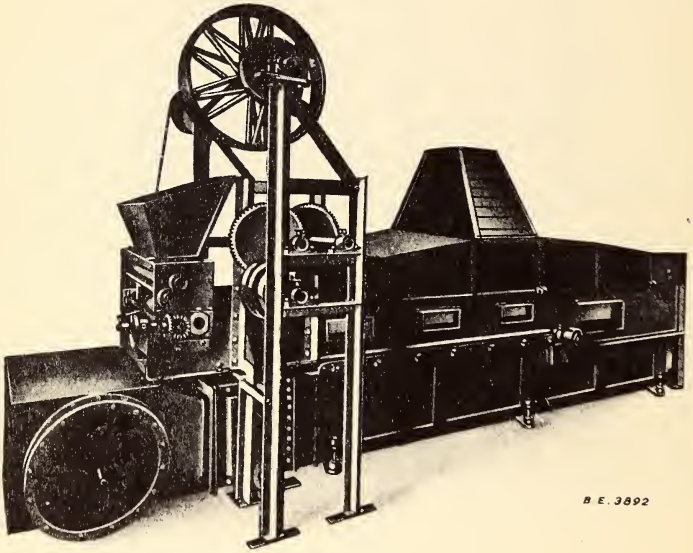
the casein. The mass of curd is spread in a 4 cm. layer and is exposed to a current of hot air under continuous agitation. In such a machine of about 1000 liters capacity, the curd of about 3,500 liters of skim milk can be dried within 3.5 hours in one procedure and without the necessity of a control or additional work. To produce one kg of dry casein the dryer consumes about 0.35kg of coal.



Drier for Acid Casein (Bergedorfer Iron Works)

On the following page, another drier is shown for the drying of rennet casein and of acid casein. This drier, although more expensive than the one previously described, is suitable for all types of casein. It is constructed as a completely automatic tunnel drier. One worker can operate several such machines. The casein is put in through a horizontal mill which is adjustable and serves as a distributor. The distance between the two rollers determines the grain size of the curd. After passing the mill, the curd falls on a metal cloth through which a current of air passes from below; underneath this cloth there is a second and similar one which is tighter and carries the first. The movement of the casein is brought about by some sort of a rake which consists of coarse, parallel wires of about 4 to 5mm length which are separated from each other by about 30-40cm, and which scrape over the surface of the cloth on which the casein is spread out. Thus the grains are lifted up and caused

to move forward. After the metal wires have covered the entire length of the cloth they return in reverse direction over the casein, until they reach again the anterior end. In the tunnel system, the drying should be interrupted after half the time. The outer surface of the casein cake dries first. If it were completely dried, and if the cake were not broken up as a precaution, the inside of the cake would remain in the original state and no homogeneous product could be obtained. In the apparatus just shown, a grinder is inserted which breaks up the casein and spreads it out again on the cloth situated a little lower. Since the chamber has windows, the casein can be exactly controlled while it passes through the machine. The medium size drier with an hourly output of 30kg of dry casein has a length of 5m. The casein remains in this apparatus for only 35-45 minutes. The coal consumption per kg casein is about 0.5kg.



Drier for Acid and Lactic Casein
(Bergedorfer Iron Works System)

Besides the acid casein and the rennet casein there are casein derivatives, namely brominated casein (with a bromine content of 12%), a nitrocasein which is obtained by the action of nitric acid, a casein xanthogenate using carbon disulphide, a methyl casein from methyl iodide, etc...

Completely pure grades of casein are acidified with acetic or lactic acid or with a mixture of 1 part of normal

hydrochloric acid and 2 parts of normal acetic acid. However, the use of hydrochloric acid is always dangerous if too much acid is being used; this must be avoided, by all means, for edible caseins. Caseins produced with hydrochloric or sulphuric acid should be washed twice with water before using them, in spite of the washing in the casein factory. The following requirements for a good acid casein are taken from the German standard specification:

REQUIREMENTS AND TESTING METHODS FOR LACTIC ACID CASEIN

There are two types of casein, namely acid casein and rennet casein.

Acid casein is either obtained by natural acidification (lactic acid: pure culture or self-souring) or by artificial addition of acid (sulphuric or hydrochloric acid) from the skim milk. For the production of casein adhesives, nowadays lactic acid casein is almost exclusively used.

Rennet casein is formed from fresh or preserved skim milk by a process of fermentation (addition of calf's rennet.) Rennet casein serves mainly for the formation of casein synthetic resins (Galalith, Akalit, etc...) It is clearly distinguished from the acid casein by its properties.

Commercial grades of lactic acid casein

Lactic acid casein is furnished in the following commercial grades:

1. Unground,
2. Ground.

Ground casein has to be below a certain mesh and is classified as follows:

Grade of Casein	Grades of Fineness Passing through the following screens:			
	German Standard		French	English
	Screen number	Mesh per square cm.	inches, mesh per inch	inches, mesh per inch
Coarsely Ground	6	36	22	20
Medium Coarse	12	144	40	35
Fine	24	576	80	65
Very Fine	30	900	95	80

To guarantee a standard fineness of grinding, a definite lower limit of mesh through which the casein will pass and an upper limit of mesh through which it will not pass, may be arranged.

Note: In the following table screens are compared according to the different scales which correspond with each other in the width of their mesh. The width of the mesh of these screens based on the French or the English in. can change within certain limits for the various products according to the strength of the wires used. Values given for these screens correspond to good average values from investigations of the Chemical Laboratory for Clay Industry, Berlin N W 21, Dreysest. 4.

Comparison of Various Screens

Inner width between mesh in mm	German Standard Screen no.	mesh per sq.cm.	Sieves based on 1 French inch = 27mm, mesh per inch	1 English inch = 25.4mm, mesh per inch
1.02	6	36	22	20
0.75	8	64	30	25
0.60	10	100	35	30
0.54	11	121	37	32
0.49	12	144	40	35
0.43	14	196	50	40
0.385	16	256	55	45
0.300	20	400	70	60
0.250	24	576	80	65
0.200	30	900	95	80
0.150	40	1600	130	110
0.120	50	2500	160	135
0.102	60	3600	180	160

Color: Casein is white, or pale yellow to butter yellow. Darker particles should occur but rarely. Casein furnished to the paper industry should only contain traces of dark particles.

Unground casein should contain only a small amount of lumps of brownish color and no lumps of reddish brown color.

Impurities: Casein must be free of impurities of any kind.

Odor: Casein should have a faint milk odor; it should not have a strongly acidic, rancid, or cheeselike odor.

Taste: Mild, not strongly acid.

Composition: Lactic acid casein should correspond to the following requirements:

Analytical Constants of Lactic Acid Casein

Ingredients of Casein	Based on Commercial Casein (assuming 10% average moisture content) %	Based on Anhydrous Casein %
Protein, minimum	78	86.7
Water, maximum	12 in commercial casein	
Ash, maximum	4	4.4
Fat, maximum	3	3.3
Acidity of 1g of casein, maximum	12.5 cc of N/10 caustic soda	13.9 cc of N/10 caustic soda

Viscosity: The viscosity should be at least 1.4 degrees Engler at 40°C. in a 12% solution with borax.

Storage: Casein must be stored in dry, cool, and well-aired rooms, separated from other strongly odorous merchandise. It can thus be stored up to 1 year without losing its quality. However, large amounts should not be stored for a long period of time during the hot summer months. The storage rooms should be cleaned thoroughly shortly before filling them with new material. If parasitical insects are found in it (Australian Thief Beetle, moths etc...), repeated monthly straining of the casein is suitable and sufficient.

Simple Testing Methods

1. Testing for Odor: 5 grams of casein are stirred up with 10cc of water. The odor of the stirred casein should be faintly milk-like, and not acid, rancid, or cheese like. The odor can also be checked while testing the borax solubility.

2. Testing for Borax Solubility: Good lactic acid casein, such as is suitable for the production of cold glues,

is easily distinguished from rennet casein by the following test, since it is almost completely soluble in borax solution, whereas rennet casein does not dissolve under these circumstances.

15 grams of casein coarsely or more finely ground are stirred up in a 200cc beaker or glass with 60cc of pure water. After soaking for at least 2 hours, a hot solution of 2.3 grams borax ($Na_2B_4O_7 10 H_2O$) in 15cc of water is added with good stirring. This is about 15% of the casein used. The mixture is heated on a water bath at about 50°C. for 10 minutes under steady stirring with a glass rod. The casein should swell up more and more under this treatment and finally dissolve completely. Poor casein is only incompletely dissolved with formation of lumps, which swell only, but do not dissolve even on careful stirring with the glass rod.

The solution should be viscous when cooled to room temperature. Its odor should correspond to the requirements given above.

Good casein should not show undissolved and glassy particles when making a film of its well stirred solution on a glass plate.

In this test, larger admixtures of dirt, sand, etc... will settle down to the bottom of the beaker or glass. These can be tested more thoroughly after diluting and dissolving with hot water as well as decanting the casein solution.

Detailed Testing Methods

1. Test for Moisture: Three grams of well ground casein are dried at 100-105°C. for six hours in a drying oven. The weighing is done after cooling in a desiccator which is filled with fresh concentrated sulphuric acid or phosphorus pentoxide.

2. Test for Ash: Three grams of powdered casein are ashed in a porcelain crucible (not in a platinum crucible) by means of a Bunsen burner. The ash is heated red hot with a blow pipe until the weight remains constant. If poorly burning carbon has formed, it is recommended to extract with water in the known manner, and to ash separately.

Acid casein is much more difficult to ash than rennet casein. The ash of the acid casein forms a glassy fusion, that of the rennet casein is powdery. The ash of acid casein amounts to about 2 to 4%, that of rennet casein to about 6 to about 9%.

3. Test for Proteins: One gram of casein is heated for about 15 minutes with about 20cc of concentrated sulphuric acid free from nitrogen and about 1 gram of mercury or copper sulphate (which latter is cheaper) until solution has occurred. 20 grams of potassium sulphate free from nitrogen are added and the mixture is heated further. When discoloration has started, the mixture is boiled for 15 more minutes and to the dissolved mass, 250cc of water are added and the whole is cooled. Thereafter 80cc of caustic soda (specific gravity: 1.30), 25cc of an aqueous solution of potassium sulphide (50 grams potassium sulphide per liter) to precipitate the mercury, and some zinc filings, to prevent bumping, are added. The flask is now connected as quickly as possible with a condenser and the ammonia which has formed is distilled off completely. The boiling time necessary for this is, as a rule, about a half hour.

It is recommended to run a blank to test the reagents.

The percent of nitrogen thus found multiplied by the factor 6.39, for casein, gives the percentage of protein (free of ash, water and fat) in the casein.

If urea or other nitrogen compounds are present, the protein content thus found is not correct. This testing method does not distinguish the content of nitrogenous decomposition products of protein which are valueless for most uses of the casein.

4. Test for Starch: 0.1gram of casein which must be finely powdered or ground are stirred up with 1cc of water on a watch glass. One drop of normal iodine-potassium iodide solution is added and the whole stirred up again. The solution must turn pure yellow. Even if there are only very small amounts of starch in the casein, the solution turns to a dirty greenish-gray to bluish color. The safest way to check the color is to put the watch glass with the sample on a piece of white paper.

5. Test for Fats: 1 gram of finely powdered or ground casein is weighed exactly in a beaker and 10cc of hydrochlor-

ic acid of the specific gravity of 1.125 are added. The material is dissolved completely over an open burner under a hood, shaking cautiously, and is then poured into a graduated test tube. The beaker is rinsed at first with 10cc of hot water, thereafter with 10cc of 96% alcohol. The wash liquors are added into the tube and shaken up well. 25cc of ethyl ether are added into the beaker and from there into the tube. The tube is now sealed and the liquids in it are mixed by shaking; the ether layer will separate only poorly if the mixture has been shaken too strongly. In the same way 25cc of petroleum ether are added. The tube is allowed to stand until the petroleum ether layer has separated entirely. The height of the layer is read and a measured volume of it is pipetted off into a weighted flask.

The ether layer containing the fat is evaporated on the water bath and under a hood, dried in a drying oven for 3 hours at 100°C. It is then cooled in a desiccator, and weighed. The flask is now dried once again and weighed again for control.

Considering the amount of casein used, the volume of the ether and petroleum ether layer read, and the volume of the fat solution pipetted off, the percent of fat of the casein can be figured out.

6. Test for Acidity: One gram of ground casein is weighed into an Erlenmeyer flask. 25cc of N/10 sodium hydroxide are added from a pipette with shaking. The flask is stoppered and the shaking is continued until the solution is complete. This usually takes a few minutes. The stopper is now removed and solution adhering to it is washed off into the flask by means of distilled water. 100cc of distilled water and 0.5cc of a 1% solution of phenolphthalein as indicator are added. The solution is quickly titrated with N/10 hydrochloric acid, shaking the flask violently. This must be done to avoid precipitation of the casein by the drops of the acid.

The number of cc. of N/10 sodium hydroxide which are used up by one gram of casein (according to this back titration with hydrochloric acid) is called acidity (neutralization value).

Lactic acid caseins show an acidity of 8.8 to 13cc. Rennet caseins have 1.6 to 2.8cc acidity.

To determine the true actual acidity it is recommended to determine the hydrogen-ion concentration. Compare M. Schulz, The Determination of Acidity in Casein, Molkerei-Zeitung, Hildesheim, No. 53,1930.

7. Test for Lactose: 10 grams of casein is put into a porcelain mortar without loss. It is moistened with hot distilled water and ground with a pestle. More hot water is added and after settling out, the supernatant liquid is transferred through a funnel into a graduated flask of 500cc capacity. The balance is stirred up again with distilled water, and after doing so 3 to 4 times, everything is transferred into the 500cc flask until this is filled to one half volume. After cooling, 10cc of copper sulphate (Fehling solution #1, see below) and 15cc of N/4 sodium hydroxide are added with shaking, and distilled water is added (15°C.) up to the mark, and the whole is shaken as well.

After the casein has settled out, the solution is filtered through a folded filter (the filtrate must be brilliantly clear), and the sugar content is determined.

25cc of Fehling solution #1 and 25cc of Fehling solution #2 are heated to a boil with 25cc distilled water. 50cc of the sugar solution, corresponding to 1 gram of casein, are added by pipette. After boiling six minutes, filter through a previously weighed and prepared Berberich funnel by means of a suction pump. Rinse with hot water, fill the funnel once with alcohol and once with ethyl ether, (to dry better and more quickly). The funnel with the copper oxide is dried thereafter in a drying oven for 25 minutes at 100°C. It is weighed after cooling, and the lactose content is figured out. In the following formula, an allowance is made for the fact that one tenth of the original weight of 10 gram, that is one gram of casein, has been used for the sugar determination.

Cuprous oxide found in grams X 0.6482 X 100 = % Lactose.

The Fehling solutions used for the lactose determination are prepared as follows:

Fehling Solution #1

Fehling copper solution: 69.26 grams of copper sulphate, purified by repeated recrystallization, are dissolved

in water in a 1000cc flask which is then filled up to the mark.

Fehling Solution #2

346 grams of potassium sodium tartrate (Rochelle salt) and 103.2 grams of sodium hydroxide are dissolved in water in a flask which is filled up to 1000cc. Both solutions are kept separately.

8. Test for Viscosity: The viscosity value does not allow an evaluation of the casein, as can be done with oils or with hide-, bone-, and leather glue, but it has some importance, inasmuch as it gives a certain control for its quality and as it falls below a certain minimum value for poor casein.

15 grams of ground casein are soaked for several hours with 35cc of distilled water, preferably over night, in an Erlenmeyer flask. The flask is put on a water bath at 40°C. 3 grams of borax are dissolved in 18cc of distilled water on a boiling water bath, cooled to 40°C and the borax solution is added to the casein. The temperature is elevated quickly to 70°C. with stirring until all casein is dissolved, which normally takes about one quarter of an hour.

After the solution is made, 72cc of water at 40°C. is stirred into it, until a completely smooth solution is formed. This 12% solution is filtered through a double layer of fine bandage-gauze before taking the viscosity determination.

The viscosity value is determined with this solution in the Vogel-Ossag-viscosimeter or in the Engler apparatus at 40°C. The viscosity values obtained in these two apparatus agree sufficiently well for practical purposes.

For complicated mixtures, e.g. in liquid casein adhesives or in paint binders, the viscosity value allows no conclusion on their quality and usefulness.

Concerning the adhesive power of caseins which is of great importance in the colored paper industry and in the printing paper industry, S.P. Gould published an interesting article in Industrial And Engineering Chemistry, No. 9, pg.1077, 1932. He writes, that the various caseins have shown differences in manufacture which cannot be explained

by chemical analyses or by physical tests. However, to have some kind of a test, as to whether a casein differs from another or not, the author used the optical rotation method, and determined the specific rotation of 15 commercial caseins. As a comparision he used a Hammarsten casein. To form his solutions he used a 10% solution of sodium acetate. 5 grams of sodium acetate were always dissolved in 40-42cc of water, 1 gram of casein was added and after allowing the mixture to stand for $2\frac{1}{2}$ hours, it was heated on the steam bath for 20 minutes. If the casein particles were not dissolved completely, the heating was continued, until all salt was dissolved. Filtercel was added to the solution and it was filtered repeatedly through a Gooch crucible with asbestos and Filtercel, until the solution came through clear. After washing the residue, filtrate and wash liquors were filled into a graduated flask of 50cc and filled up to the mark. These solutions containing 2% of casein and 10% of sodium acetate were polarized at 30°C. The specific rotation was calculated for anhydrous casein free of ash (moisture and ash were determined in advance). The average values are shown in the following table:

Specific Rotation $[\alpha]_D^{30^C}$ and Adhesive Power of Commercial Caseins

Hydrochloric Acid Caseins

Sample	Specific Rotation	Adhesive Power
1	-72.6	9
2	-85.9	9
3	-77.5	9
4	-80.4	9
5	-87.0	10
6	-92.2	10
7	-72.6	11
8	-83.7	9
Average	-81.5	

Lactic Acid Caseins

Sample	Specific Rotation	Adhesive Power
9	-81.3	9
10	-75.4	9
11	-74.4	10
12	-80.7	11
13	-89.9	11
Average	-80.3	

Sulphuric Acid Caseins

Sample	Specific Rotation	Adhesive Power
14	-61.7	10
15	-72.2	11

The average values of hydrochloric acid and of lactic acid casein agree practically, The average values used for sulphuric acid caseins, however are considerably lower. This might perhaps be explained by the fact that the solutions were somewhat cloudy and difficult to polarize. There were no relations found by Gould between adhesive power and specific rotation. Tests on the influence of overheating of the casein showed that the casein molecule is not influenced at 90°C, although by heating the casein becomes more difficult to grind and to dissolve.

CHAPTER II

CASEIN ADHESIVES

Casein has become exceedingly important for the production of casein adhesives. The knowledge that curd gives a viscous and very water resistant adhesive dates from the 11th century, when curd was used mixed with slaked or unslaked lime. During the centuries, this simple mixture was more and more improved and sometimes made up together with other adhesive materials, as for example in the plywood industry (mixtures of casein with blood albumen). The wood-working industries have the greatest need for casein glues. There are numerous other applications of straight casein glue or of mixtures of such glues which I shall treat later on.

It is not correct that only lactic acid casein is suitable for the casein glue production. Hydrochloric acid casein and sulphuric acid casein are also useful for this purpose, if they are washed out repeatedly with water before dissolving them in alkalies.

If acid casein is stirred into water, it is not dissolved but only swells more or less after standing several hours. To bring out the adhesive properties of the casein, a dissolving agent for the casein must be added, in first class alkalies. There have been suggested various dissolving agents for the casein and for the various compositions of glue; some of these agents are absolutely without practical value; some differ among each other only very little in their efficiency; some of them have good dissolving action, but have a number of other disadvantageous properties, such as too quick thickening of the glue, discoloration of the wood, lowering of adhesive power or of water resistance etc... It should not be forgotten that the purpose for which the glue is used is very essential that is that a glue does not offer any difficulties in one case, but is completely useless in another. Which dissolving agent should be used for the casein in each case, or what mixtures of dissolving agents should be applied, must be

found by practical experience. A very interesting article about the analysis of powdered casein adhesives has appeared by Dr. H. Pfanner in "Gelatine, Leim, Klebstoffe", No. 5/6, pg. 100-102, 1936.

The first question for the manufacture of a casein adhesive, or one of the casein paint binders treated later on, is what grade of casein should be used. Should it be a casein which gives high or low viscosity in solution, and should it be quickly or slowly soluble?

In general, the rule holds that the solution of the casein increases proportionally with the amount of sodium hydroxide added. Experiments by Cohn and Hendry, published in Journal Gen. Physiology, vol. 5 pg. 521, 1923, show that the casein is a stronger acid than carbonic acid and that it frees the latter out of solutions of carbonates and bicarbonates. How strongly acid the casein reacts, is shown by the following comparison of pH values of a casein solution, with dilute acid and alkaline solutions:

Normality of Solutions	HCl pH	H_3PO_4 pH	NaOH pH	NH_4OH pH
0.001	3.00	3.05	11.00	10.11
0.005	2.30	2.46	11.70	10.46
0.010	2.00	2.23	12.00	10.62
0.050	1.32	1.74	12.68	10.97
0.100	1.02	1.55	12.97	11.12
0.500	0.36	1.02	13.62	11.48
1.000	0.10	0.76	13.88	11.62

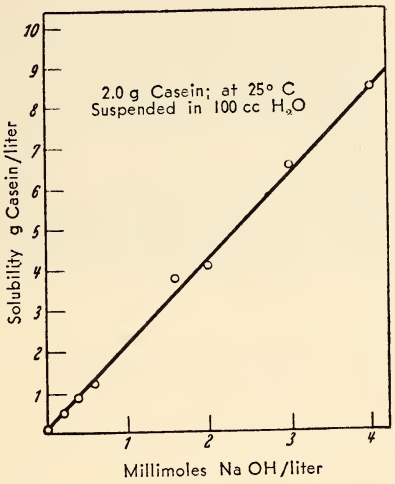
This comparison is important for the dissolving agents for casein which will be treated later, because it shows how different the action of alkaline solutions on the casein is from that of the acids. In acids the casein dissolves only after it has reached a certain swelling limit.

As an example of the action of one of the most important dissolving agents for casein, namely caustic soda, the following graph is shown:

This graph proves distinctly the rule mentioned before, that the solubility of the casein increases proportionally with the amount of caustic soda added.

Similar conditions are true for the other dissolving agents for casein such as caustic potash, lime, ammonia, sodium alphanaphthalene-sulphonate, soda ash, borax, sodium bicarbonate, trisodium phosphate, sodium silicate, etc...

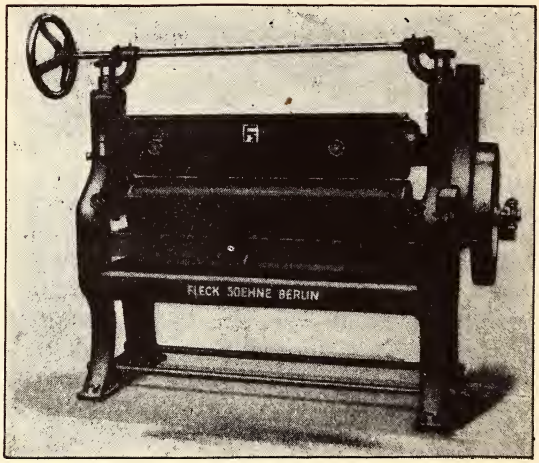
By the choice of certain dissolving agents, one can change the solubility of the casein and the viscosity of the finished solution. By the choice of a casein dissolving with low or high viscosity, the amount of casein in the casein solution can be changed This will influence considerably the quality and price of the finished casein glue.



Relationship between Amounts
of Casein Dissolved and Alkali
(Sutermeister-Cohn-Hendry)

The best casein glues are naturally obtained from low viscosity casein. Such grade gives adhesives of high adhesive power which nevertheless can be easily brushed on or put on in gluing machines. Caseins of very low viscosity which dissolve quickly and easily are the lactic acid caseins.

It is not possible, however, to obtain a certain casein for a certain purpose or if the various casein shipments differ, it is necessary to conform to these facts. The required viscosity of the casein glue has then to be obtained by a choice of the dissolving agent, since simple dilution changes the adhesive power.



Adhesive Spreading Machine Used
in Plywood Factory

According to determinations of Sutermeister, 3 glues of equal consistency can be obtained from the following formulae:

1. 100 grams of casein are soaked in 300 grams of water, and 8 grams of sodium hydroxide are added.

2. 100 grams of casein are soaked in 600 grams of water, and 4 grams of sodium hydroxide are added.

3. 100 grams of casein are soaked in 600 grams of water and 13cc of ammonia (28-29%) are added.

In the experiments 1 and 2, part of the amount of water mentioned for the soaking of the casein are used to dissolve the sodium hydroxide. In experiment 3, the ammonia is diluted with some of the water, and is thus added to the casein soaked in the balance of the water. These 3 glues show almost equal viscosity, but it was shown that no. 1 dissolves in only 10 minutes, whereas no. 2 needs about $\frac{1}{2}$ an hour, and no. 3 an hour to dissolve. Ammonia, furthermore, has a strong thickening action on low viscosity caseins. It is possible to make very viscous solutions with little casein from ammonia and low viscosity caseins. A similar action is exerted by ammonia upon borax-shellac solutions. The long dissolving-time of experiment 3, using ammonia, can be shortened considerably by heating the mixture, or by using hot water when making it up.

The glues mentioned can, of course, be made only in liquid form (wet-mix). To make them up as "prepared glue" powders, the sodium hydroxide given in formula (1) and (2) has to be replaced by calcium hydroxide and by another addition which will react later on in water with the calcium hydroxide, forming sodium hydroxide. Such a composition is as follows:

100 grams of Casein
7.4 grams of Calcium Hydroxide
0.2 grams of a Sodium Salt, such as Sodium Carbonate, Sodium Oxalate, Sodium Tartrate, Sodium Citrate, Sodium Salicylate, Sodium Phosphate, Sodium Fluoride, Sodium Sulphide, Sodium Arsenate, Sodium Arsenite, Sodium Stannate, etc...

100 grams of this mixture require 300 grams of water to form the finished casein glue. Such a glue remains workable,

after being dissolved in water, for 8 to 10 hours. However there is no free lime present in this glue, because all the calcium hydroxide has been transformed into calcium salt. It is possible, however, to use sodium hydroxide in prepared glue powders for which it normally is not suitable because of its hygroscopicity under atmospheric conditions. This is done by using sodium salts which will hydrolyze only after the powder is dissolved in water. Such salts are, according to Edwin Sutermeister: borax, soda ash, trisodium phosphate, sodium fluoride, sodium sulphide, sodium arsenate, sodium arsenite, sodium stannate, sodium tungstate and the sodium salts of various weak organic acids. Aluminum sulphate also gives excellent powdered glues in combination with casein, lime hydrate, and sodium carbonate. The following table by Sutermeister shows what amount must be added to obtain equal results:

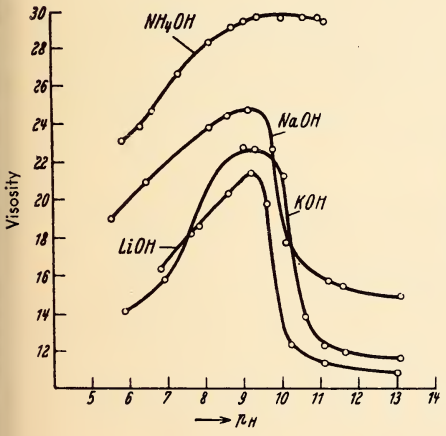
100 grams of casein and 600 grams of water require the following amounts for solution:

Salt	Amount of Salt in Grams
Borax	14.7
Sodium Phosphate	12.3
Sodium Stannate	20.0
Sodium Carbonate	16.0
Sodium Arsenate	30.0
Sodium Fluoride	64.0

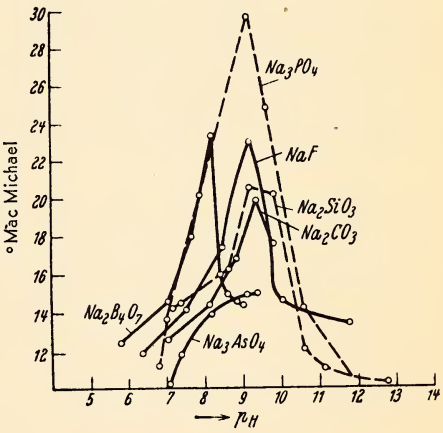
To dissolve with sodium fluoride, heat is necessary.

If sodium hydroxide were used instead of any one of the salts mentioned, only 3.95 grams would be necessary to dissolve the casein but the solution would go very slowly. Heating to 60°C. will, however, cut this time to a few minutes. In the way just mentioned one could, of course, make powdered glues, too. But to dissolve the casein powder in the water at room temperature would require larger amounts of the above mentioned salts, otherwise this would take too long. The solution can be speeded up if a very fine, though not too fine a casein be used, namely one that will pass through a screen of 400-900 mesh. According to the information of a large casein importer at Hamburg, the casein-glue industry works almost exclusively with a finely ground grade of alkali-soluble casein of 60 mesh per inch (Screen No. 20)

In using caustic soda, small deviations considerably influence the consistency of the glue. With the salts mentioned above, the danger is not so great. It should be taken care, however, that the pH value of the glues is not higher than 10, if possible, in order to make the glues stable for some days and prevent them from becoming too thin and retain as much as possible of the adhesive power which is unfavorably influenced by progressive hydrolysis. The influence of alkalies and hydrolysable salts on the viscosity of casein is compared in an article by Zoller in Journ. Gen. Physiol. vol. 3, pg. 635, 1920 and is shown in the following two tables. Casein is decomposed at a pH value of 10.5 or higher and the casein glue loses its adhesive properties. Casein glues therefore must be kept below these values. As the graphs show, a viscosity maximum is only given by borax at pH 8.1, but it can also be seen that much more sodium fluoride can be used to get a pH of 9 than sodium phosphate. This is important because of the quick solubility of the casein.



Variation of Viscosity of 9% Casein Solutions with Change in pH of Various Alkalies



Variation of Viscosity of 9% Casein Solutions with Change in pH of Various Hydrolysible Salts

To make the casein glue water insoluble after the drying, chromium peroxide, acetaldehyde, tannic acid, chromium potassium sulphate and formaldehyde (U. S. Patent 1,964,960 uses paraformaldehyde for glues in hot pressing) are used. The alkali caseinate may also be transformed into the caseinate of a heavy metal (by adding ammoniacal solutions of copper, tin, zinc, chromium, or magnesium, salts to an ammoniacal casein solution) - or of an earth alkali metal. As one of the latter, calcium caseinate is used in actual practice, since the use of lime is not only cheap but also very suitable, since the lime hydrate is easily dissolved. Furthermore, the addition of sodium resinate gives a very moisture resistant glue, and use is made of this addition when, for instance, a label glue resistant to heat and moisture is made from casein, borax, sodium resinate and water. An addition of furfurol can be made successfully to casein glues. Furfurol resinifies slowly in aqueous alkaline solution, just as synthetic resins are formed from furfurol with phenol and alkali. The more concentrated the alkali, the quicker is the transformation of the furfurol. Addition of furfurol considerably retards the thickening of the casein glues. To retard the thickening of the glues which takes place when adding formaldehyde, one can add ammonia, aluminum acetate, glycerine, borax, or dextrin. Similar effects as that of formaldehyde are gotten by trioxymethylene, but it does not gel up the glue as quickly. The following formula is an example of such a cheap casein glue which turns water resistant:

About 100 grams of casein are stirred into 200 grams of water, and are allowed to soak. 11 grams of sodium hydroxide are now dissolved in 50 grams of water and the solution is added to the casein suspension with stirring. As soon as the casein is completely dissolved, 20 grams of calcium hydroxide is added. A glue of this kind will remain liquid for about 7 hours. This glue must, of course, be made up immediately before use, because of its liquid form. This gives very water resistant stable wood gluings. Of course it is easily possible to use volatile bases, such as ammonia, instead of the caustic soda which would remain in the glue. Casein glues made with ammonia, although more water resistant after the drying than those made with caustic soda, suffer by the fact that they are very viscous and difficult to apply. The glue also decomposes readily. This can be retarded by lowering the amount of calcium hydroxide used, but in this case the water resistance of the glue after drying will suffer. It is a known fact that

with the increase in content of lime hydrate the water resistance of the glue will increase and the time of its workability will shorten. All casein glues of any composition whatsoever are the less water resistant the longer they are stable. This observation has been proved again and again by innumerable experiments.

A powdered casein glue, made from 100 grams of casein and 30 grams of lime hydrate, made up with water in the ratio 1:3 would give an excellent water resistant glue, but unfortunately its transformation goes so quickly that the glues solidifies after one to two hours. To prevent the premature setting of a casein glue thus made water resistant, the glue must be kept more alkaline by addition of one or more of the sodium salts already mentioned. By this the glue becomes stable enough to stay liquid for about 8 hours. Of course one can keep the glue liquid for some time without the addition of a sodium salt, by simply increasing its water content. However, a glue of such low viscosity can often not be used in practice. A glue thus diluted, may be made more viscous by the addition of alum or calcium chloride, but such an addition can only be made after dissolving the glue powder in water, that is directly before using. This makes the method difficult and hard to control. Reagents which retard the quick thickening of the casein glue are sodium bisulphite, ammonium bisulphite, and particularly acids, such as oxalic acid. The following table gives the length of working life of a glue made with lime hydrate:

Composition of the glue: 100 parts of casein, 250 of water, 100 of water plus calcium hydroxide in the amounts given below, furthermore 70 parts of sodium silicate

Parts calcium hydroxide in the glue given above	Working life of the finished glue, in hours
9	48
12	20
15	16
22	11
27	4
35	3
60	1 3/4
100	2 1/4

As a standard, an amount of 30 parts of lime per hundred parts of casein can be assumed. If less is taken, the water resistance suffers. If more is taken, the water resistance does not increase considerably, but the stability is shortened too much. It is completely up to the manufacturer to make a glue from 100 parts of casein and 30 parts of lime more or less stable, by adding more or less sodium salts and particularly by choosing certain sodium salts.

Regarding the use of sodium phosphate, the comparison of two typical recipes for disodium phosphate and trisodium phosphate is enlightening:

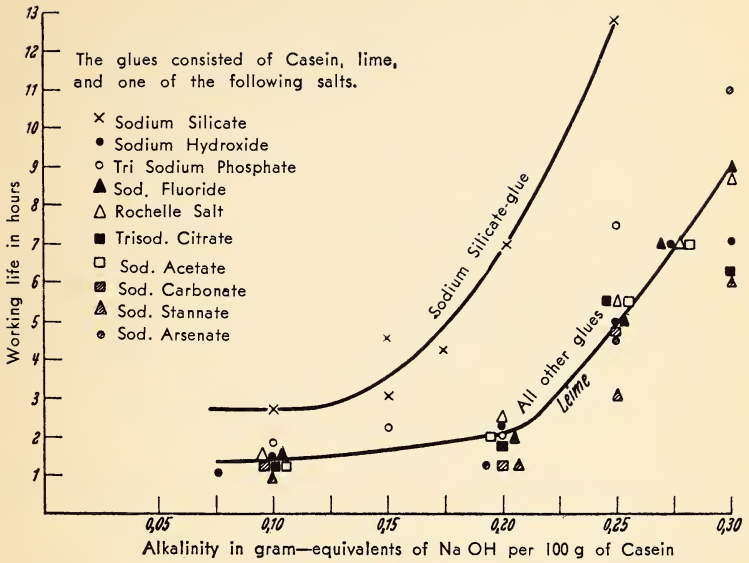
Casein Glue with Disodium Phosphate

11 parts by weight of disodium phosphate is dissolved in 110 parts of water. 30 parts of a 10% caustic soda is added, whereby the same effect is gotten as with trisodium phosphate as a starting material. This solution is reacted with a mixture of 100 parts by weight of casein and 300 parts by weight of water at water bath temperature, until the mass has the necessary consistency. This is diluted for use with 300 additional parts of water. As a correct mixing ratio of disodium phosphate to casein in the formation of casein cold glues we can assume 6:70.

Casein Glue with Trisodium Phosphate

100 parts of casein are mixed with 30 parts of lime hydrate and 2 parts of mineral oil to prevent dusting and premature reaction between the ingredients, and 15 parts of trisodium phosphate ($Na_3PO_4+12H_2O$.).

The ingredients have to be mixed well, and the powder should be stored dry. For use, 150 parts of this powdered glue is mixed with 300 or more parts of water, according to the consistency desired.



Relation between Alkalinity and Working Life
Casein Glues. (Sutermeister)

As can be seen from the graph given on the previous page the glues made up using sodium silicate have a particularly long working life, and therefore extensive use is made in the plywood industry of the addition of sodium silicate. It is, however, emphasized by various experts, that the glues become particularly hard because of the addition of sodium silicate. One says, they petrify. This is a disadvantage, because it wears off the tools (planes, saw blades, etc...). The often uttered opinion that sodium silicate keeps the glued plates moist longer, because of the moisture in it so that these do not dry out before they pass through the press, is not correct, because this is not caused by the moisture content of the sodium silicate but by its retarding action. This is demonstrated by the fact that the addition of sodium silicate as a powder has the same effect as has liquid sodium silicate. Its action, retarding the setting, is based on the content of colloidal silicic acid in the sodium silicate. The presence of silicic acid extraordinarily delays the setting of the casein glue. Sodium silicate of 40°Bé is the most suitable, since its sodium is present in the form of meta silicate, and the ratio of sodium oxide to silicic acid is 1: 3.25.

The following shows the composition of a casein glue based on sodium silicate as an example.

100 grams of casein is soaked in 250 grams of water. 20-30 grams of lime hydrate is separately dissolved in 100 grams of water and the solution is added to the casein with stirring. When the casein is dissolved 70 grams of sodium silicate is stirred in. If the lime content of this mixture is varied the stability of the glue changes as shown by the graph.

Although casein glues with sodium silicate do not show too high an alkalinity and therefore cause little discoloration of the veneer (even oak does not discolor below a pH of 8), it is often desirable to keep the glue stable for more time than just a few hours. If one tried in this case to get this by lowering the lime content, the water resistance of the gluings would naturally suffer. Therefore one increases the water resistance (diminished by lowering the lime content) by adding copper chloride. The time of applicability can also be lengthened by adding animal glue to the casein. According to information of the United States Forest Product Laboratory such a wet-mix glue, consists of:

100 grams of casein, soaked in 220 grams of water. 20-30 grams of lime hydrate is stirred up with 100 grams of water and added into the casein. After stirring until the casein is dissolved, 70 grams of sodium silicate is added and finally, a solution of 2-3 grams of copper chloride in 30 grams of water is stirred in. At first, green copper hydroxide precipitates, but this need not be disturbing because the color of the glue soon changes to violet and the glue is ready for use. The copper chloride may also be added to the casein while this is soaking. A glue made this way is said to have good water resistance, and has been used successfully for many years in the plywood industry. Sometimes copper sulphate is used.

Besides the main ingredients of a casein glue, namely casein, lime hydrate, water and sodium salt, other additions are made to give other or better properties to the glue. As mentioned before, formaldehyde is used to make the glue water resistant. A glue of this kind thickens too fast, however, and becomes useless. To prevent this very quick setting, infusorial earth or China clay or one of the previously mentioned materials may be added. The presence of silicic acid prevents premature gel formation in the casein glue, as mentioned in connection with sodium silicate. In this case 1.250kg of formaldehyde diluted with water is used for 100kg of dry casein and is added into the finished casein cold glue. A glue of this kind remains useful for about 8 hours. If one doesn't expect an immediate resistance to water from the glue, less formaldehyde may be taken. In this case the dried glue film will become water resistant a few days later. Hexamethylenetetramine which forms formaldehyde on heating is also used. Paraformaldehyde or a mixture of urea with formaldehyde, being odorless and splitting off formaldehyde at 70°C, can be used with advantage. That is, one may add this hardener to a glue for the hot pressing, causing hardening at 80 to 110°C. Such formulae are protected by the Austrian patent 147,807 of R. Silberger. Polyhydroxymethylenes, such as trioxymethylene, are present in many glues as hardening agents.

Another addition is that of glycerine, favored by plywood factories to prevent drying of the glued plates before they are passed through the presses. The same effect may be gotten by urea which is cheaper. There is much discussion over the addition of sodium fluoride, mentioned before, of which many glue experts say that no good liquid glue can

be obtained without it. It is a fact that this sodium salt gives properties differing from those given by sodium phosphate. Casein glue containing sodium fluoride dissolves faster when stirred into water than one with trisodium phosphate. Whereas casein is dissolved quickly by sodium fluoride, it is dissolved only slowly by trisodium phosphate, and when stirring larger batches of the latter glue powder into water, the mass is at first too viscous for stirring. Only after some time, it thins down sufficiently to allow the use of a stirrer. It has been observed that sodium phosphates cause discolorations of the casein glue. Sodium fluoride containing glues, when rubbed between the fingers, show an adhesion typical of them, not given by glues made, for instance, with trisodium phosphate. Similar adhesiveness is obtained by the more expensive materials such as sodium stannate, tannic acid etc... One has to consider on the other hand that casein glues with too much sodium fluoride cause skin diseases, particularly if the casein glue powder is stirred in with development of a lot of dust or if the laborer handling the finished glue smears it all over his hands and allows it to stick there for hours and to dry. Used in small amounts, however, sodium fluoride has been found by many experiments to have favorable action, particularly that of causing the glue to cling quickly to the materials treated with it. In resemblance to the work with synthetic resins, where skin diseases have caused trouble, this should be blamed here as there to allergic conditions on the part of the persons concerned. Or, as sometimes reported in the technical press, there were quite different causes and the innocent glue was blamed for it. We use in the industry without hesitation much worse poisons, the elimination of which appears to be impossible and may even be unnecessary as long as the necessary care is taken in working with them.

Instead of sodium fluoride, magnesium silicofluoride and zinc silicofluoride are sometimes recommended in the literature; although neutral compounds, both react acid and possess the property to decompose in the presence of lime which, as we know, is present in casein glue. The products of decomposition are silicic acid, magnesium and zinc fluorides, and calcium fluoride, all insoluble preservatives which are weaker in action than sodium fluoride which remains soluble. Magnesium and zinc silicofluorides are crystallized products. Their finest grade is in the form of a crystalline flour. They tend to cake. I don't quite understand what their importance is, although I found a

note in the British Patent 379,320, according to which a water paint can be made with magnesium silicofluoride. 400 grams of linseed oil soap is mixed with 4 liters of water and with 75 grams of lime hydrate and in 1 liter of water. This mixture is stirred into 5 liters of a 30% solution of magnesium silicofluoride in water. The dispersion which results is diluted with 30 liters of water and put through a sieve. It is then diluted with 30 liters of water and 1 gram of tartaric acid, oxalic acid, or sodium citrate is added. The finished mixture is worked into Portland cement. The action of magnesium silicofluoride is perhaps caused partly by the magnesium, since magnesium oxide and magnesium sulphate, too, prevent the premature setting of the casein glue, that is the formation of calcium caseinate. The effect, however, cannot be as complete as one would expect as can be seen from the reflections just made. The same effect is obtained much more cheaply anyway by the addition of sodium silicate, for all practical purposes.

In the following, the formulas of the aforementioned chemicals are given:

Sodium Fluoride: NaF
Magnesium Silicofluoride: $MgSiF_6 \cdot 6\ H_2O$
Zinc Silicofluoride: $ZnSiF_6 \cdot 6\ H_2O$

It is favorable, but not absolutely necessary to spray the glue powder with petroleum or mineral oil during the preparation of the casein glue in the mixer to prevent too strong a dusting of the glue during the manufacture and while dissolving it in water. This spraying is particularly desirable when powdered sodium silicate is used in the glue, because the sodium silicate forms lumps easily when moistened. If the powdered sodium silicate were completely dehydrated before the addition to the glue, there would be the disadvantage that it then becomes exceedingly difficult to dissolve. A small moisture content in powdered sodium silicate must, therefore, be considered desirable. The spraying of the glue powder with petroleum or mineral oil therefore plays an important role to prevent lump formation of the sodium silicate in the glue. Other additions to powdered casein glues are dextrin, powdered resins, and wood flour, but their value is doubtful. The use of the latter should be condemned just as much as the addition of glue fillers, since the worker with the glue never knows exactly how much filler he may add to it for the veneer work without losing too much adhesive power. Detailed information

is given by Hadert: "Is a filling of animal glue, casein glue and blood albumen possible?" and: "Filling of sodium silicate containing glues", published in the journal "Gelatine, Leim, Klebstoffe", No. 11/12, pg. 215-219, 1935 and No. 3/4 pg. 52-55, 1936. Chalk should never be added to powdered casein glues as is often done, since it represents a mere cheating of the buyer just as in the case of the wood flour.

The production of powdered glues takes place in mixers of different construction, all of which are useful provided that they allow a truly good and thorough mixing of the powder. Gyro-mixers are excellent for the mixing of powdered and wet-mix casein glues. The walls of the vessels should not be attacked by alkalies which excludes aluminum, copper, and brass. The nearer the arms of the stirrer come to the edge and the walls of the mixing trough, the better will the casein glues be mixed.

A good casein cold glue should possess the following properties, as outlined in the German standards specifications:

Powdered (prepared) casein cold glue consists of finely powdered or medium coarse lactic acid casein which is mixed in suitable proportions with finely powdered slaked marble lime hydrate, ($Ca(OH)_2$) as well as with other suitable ingredients, such as metal oxides, hydroxides, inorganic salts, preservatives, and other additions of organic nature (oils, resins). These powdered glues are stirred up with definite amounts of water immediately before use.

Properties

1. Appearance: Casein cold glue should be dry, finely powdered or medium coarse.

2. Odor: Casein cold glue should not smell of cheese.

3. Minimum Casein Content: There should not be less than 50% commercial casein with not more than 12% of moisture in casein cold glue.

4. Moisture Content: The moisture content of casein cold glue should not exceed 16% at 65% of relative atmospheric humidity.

5. Applicability of the Glue Ready for Use: There should be formed within the time indicated by the supplier, but at least within one half to three quarters of an hour, a smooth and cream like mass free of lumps, if the casein glue powder is stirred up correctly with the amount of water specified for it by the supplier. There are, however, special casein cold glues which must be excepted from this rule and for which special specifications should be given.

6. Stability of the Glue Made Ready for Use: A normal casein cold glue should stay workable for 6 to 8 hours after mixing it up with water. Here, too, exceptions exist for special glues.

7. Joint-Making Strength of Scarf Jointed Samples under Traction: Dry joint-making strength should be at least 55kg /sq. cm.

The joint-making strength in wet condition should be at least 20kg /sq. cm.

The joint-making strength after soaking in water and drying should be at least 50kg per sq. cm., or 90% of the dry joint-making strength.

8. Plywood Shear Test: The shear resistance in dry condition should be at least 20kg /sq. cm. In wet condition, it should be not less than 7.5kg /sq. cm.

In packing these glues, care should be taken to protect them from moisture. Casein glues should be stored in air tight containers and protected from heat and too strong sun light.

Simple Testing Methods

1. Testing of Water Resistance: Five sample pieces made, according to specifications given later, in the size of 10 x 2.5 cm, are stored under water at about 20°C. for about three days, and dried in air for two days. After the drying, no cracks should show and none of the plies should separate. The plies should not separate during their immersion in water.

2. Brief Joint-Making Strength Test (Factory test): Butts 15 cm long, 0.5 cm high and 2 cm wide are made from

pinewood, and two each are glued together with their broad sides with edges of 2 cm. to form a glued surface of 4 sq. cm.

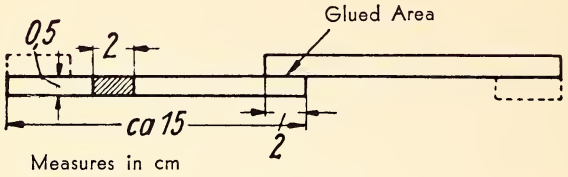


FIGURE 1

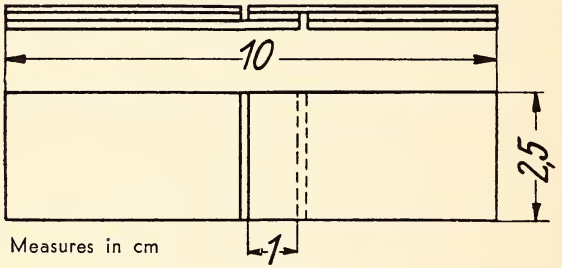


FIGURE 2

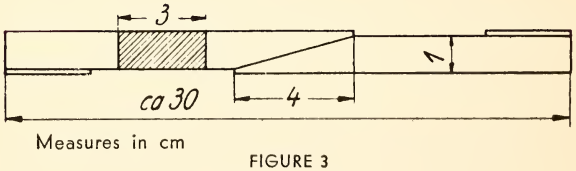


FIGURE 3

The glued rods are put into clamps and are dried for 4 days, if possible. After the drying the butts are torn lengthwise. If no testing machine is available, this is done by hanging weights on them, avoiding sudden loading, until they break apart. In this simple experiment a joint-making strength of about 40-50kg /sq. cm. can be expected.

Detailed Testing Methods

1. Test for Casein Content: 10 grams of cold glue is stirred up carefully with 70cc of chloroform in a graduate of 100cc capacity by means of a glass rod. More chloroform is added with stirring until the liquid reaches about 2cm near the upper rim. The glass rod is taken out, washing back into the graduate the particles clinging to it. The graduate is now filled with chloroform almost to its rim and is left in a cold place and covered with a watch glass over night. The casein which rises to the surface is put on a tared filter with a spoon or spatula. It is washed with chloroform and dried to constant weight in a drying oven at 98°C together with the filter, and is weighed quickly.

It may be well to investigate the material that has risen to the surface of the chloroform. This is done with a microscope and shows whether there is wood flour in the casein.

The weight found, expressed in grams, will give the percent of anhydrous casein in the glue by multiplying by ten, the percent of commercial casein in the glue by multiplying by eleven (commercial casein assumed to contain 10% of water).

2. Determination of the Inorganic Ingredients of the Casein: The casein separated by the method just mentioned sometimes contains inorganic ingredients foreign to the casein. Therefore, 3 grams of the separate casein must be ashed in a porcelain crucible over a Bunsen burner. The ash is heated to constant weight at red heat with a blast burner. It may be advisable to extract with water, if poorly burning carbon forms, and to ash separately in the known manner. If the ash content is higher than 3.5% (which is the average ash content of acid casein) the excess percentage is subtracted from the casein found in 1.) and is added to the inorganic matter.

3. Determination of the Inorganic Ingredients of the Cold Glue: The bottom precipitate in the graduate (compare 1.) contains the inorganic ingredients. It is filtered off into a tared filter, washed with chloroform, and dried to constant weight at 100°C. in the drying oven and is weighed after drying in a desiccator. The weight found, expressed in grams, multiplied by ten, give the content of inorganic ingredients in percent. Additions may

have to be made to the value found according to 2.)

4. Determination of the Protein Content in the Casein: The casein separated by the chloroform method is analyzed for protein according to the method outlined in chapter 1.

5. Determination of Joint-Making Strength of the Casein Glue on Scarf-Jointed Samples under Traction:

a) Preparation of the Glue Solution: 50 grams of well mixed powdered casein glue are stirred together with the amount of water specified by the supplier to give a smooth mass. The glue made up is used after the length of time specified by the supplier.

b) Preparation of Samples: Prepare butts from pine core wood of 3cm width and 1cm height according to figure 2. Five are needed for each experiment, that is a total of 15 sample butts with a ratio of height to length of slope of 1:4. It should be taken care that the wood fibers run parallel to the long axis of the butt. The tips of the slope cut are taken off as sketched in figure 2. The cold glue made up according to (a) is spread on the surface to be joined together avoiding air bubbles. Two sample butts each are pressed together with their glued surfaces in such a way that the slope cuts cover each other. They are kept under normal clamp pressure for 12 hours in such a way that the glued surfaces cannot move. Two small wooden plies are glued against the ends of the sample butts. They must be thick enough to correspond to the displacement of the two sample butts at the glued joint (caused by cutting off the tips of the slope cuts.) By this arrangement an eccentrical pull is not exerted on the glued joint. The samples are stored in a room at 20°C. and at about 65% relative atmospheric humidity for six days, and are then used for the tearing experiments.

c) Test for Dry Joint-Making Strength: Five of the samples made up according to section B are torn apart. The joint-making strength B in Kg /sq. cm is calculated as an average value from the results of the five tests according to the formula

$$B = \frac{P}{f} \text{ Kg /sq. cm}$$

in which

P is the weight in kg at which breaking occurs
f = 3 x 4 = 12 sq. cm is the glued surface.

Values lower than the minimum value outlined in the Standard Specifications, that is 55kg per sq. cm, may be passed as long as they are not off more than 10%, if the fracture takes place mainly because of the tearing out of early wood from the wood surfaces and if the tests according to the sections d and e give satisfactory values. If lower values than that are found, and if the tearing took place in the early wood, the entire testing must be repeated on samples with more late wood.

d) Test of Joint-Making Strength in Wet Condition: Five of the samples made according to section b are stored for 24 hours under distilled or tap water of 20°C. and are torn apart immediately after taking them out.

The joint-making strength of the glue in wet condition (figured out as in section c) is calculated as the average value obtained from the five samples and should be not less than 20kg /sq. cm.

e) Test for the Water Resistance of the Gluing: Five of the samples made as in section b are stored under distilled or tap water of 20°C. for 24 hours, are taken out and stored for 48 hours at 20°C. and at about 65% relative atmospheric humidity and are then torn.

The joint-making strength of the glue after storing in water and drying is figured out as in section (c) as the average value of all the results of the five samples, and should be at least 50kg /sq. cm which is 90% of the dry joint-making strength.

6. Determination of the Shear Resistance of Casein Glue on Plywood:

a) Preparation of the Glue Solution: see section 5a.

b) Preparation of the Samples: Three veneer plies of birch wood of at least 0.5 to not more than 1mm width and of 30 cm side length are glued cross-wise, that is in such a way that the direction of grain of the middle ply runs cross-wise to the direction of grain of the two outside plies. The glue made up according to specifications is put on with a brush distributing it equally over both sides of the center ply and over one side each of the two outer plies. The faces to be glued together are put on top of each other, are left alone for five minutes to allow

the glue to penetrate and are then pressed under 12 to 15kg. per sq. cm, preferably in a plywood press. After one hour the plywood is taken out of the press, is left for the next 24 hours under normal clamp pressure and is stored in the latter for six days at 20°C. and 65% relative humidity. The plywood plate is then cut into three strips, each about 100mm broad by cutting at right angles to the grain direction of the outside plies. From each one of these strips the samples for the tests according to section c and d are cut out in a width of 25mm each, according to figure 3 and are made, if necessary, for the simple test for water resistance (according to section 1, Simple Tests) in the dimensions of 10 x 2.5 cm.

In the middle of each sample strip small cuts of 1mm width on both sides of the plywood are made, for instance with a small saw, at a distance of 10mm from each other. Each incision cuts through two plies. Thus a glued surface of 1cm length and 2.5cm breadth (2.5 sq. cm) remains.

c) Testing of the Shear Resistance in Dry Condition: Ten of the samples made according to section b are torn. Tests in which the strip does not tear where it is glued but in the wood are not valid. The shear resistance S in kg /sq. cm is figured out as average value from at least 5 valid values according to the formula

$$S = \frac{P}{f} \text{ Kg /sq. cm}$$

in which

P is the weight in kg at which breaking occurs,

and $f = 1 \times 2.5 = 2.5$ sq. cm is the glued surface

The shear resistance of the gluing in dry condition should be at least 20 kg per sq. cm.

d) Testing of the Shear Resistance in Wet Condition: Ten of the samples made according to section b are dipped for a very short time into melted paraffin at the clamping ends and are kept under water for 48 hours. The samples are taken out of the water, dried well by means of filter paper, freed of paraffin and are torn immediately. Those tests in which the sample splits in the wood instead of at the glued surface are not valid.

The shear resistance in wet condition is figured out as in section c from the average of at least 5 valid values, and should be at least 7.5 kg per sq. cm.

As far as the preservation of casein glues is concerned, much has been written about preservation in general and the various manufacturers have published such explicit information that it becomes unnecessary to treat this field. I should like to mention the article by Friedr. von Artus about glue conservation in "Gelatine, Leim, Klebstoffe" No. 7/8, 1936, pg. 129-130, and another article by Dr. A. Herrmann about the mold resistance of casein glues, in the same journal, No. 10, 1934, pg. 224-229. In this article the testing of sodium fluoride, corrosive sublimate, thymol, arsenic, zinc sulphate, nitrobenzene, copper chloride and xylamon are treated. Useful preservatives are the parahydroxybenzoates, nitrobenzene, salol, sodium salicyate, thymol (especially recommended for crude casein), oil of turpentine, tricresol, formalin, borax, boric acid (which is said not to be as good as borax which latter also guarantees unchanging consistency of the glue, while phosphates cause thinning out), sodium fluoride, etc. The Preventols are chlorinated phenols dissolved in organic bases, forming yellowish to brown liquids which are neutral and have strong preserving power. Normally, 0.1 to 0.3% are sufficient. Preventol is at the same time a solvent for casein and therefore lowers the amount of alkali required. Another much used preservative, (because of its cheapness) is phenol. 0.6% of it is usually enough. Of formaldehyde, 2% is usually used. Sodium orthophenylphenate ($NaOC_6H_4C_6H_5 .3H_2O$) is a white crystalline powder, non-toxic and very effective. 0.5 to 1% on the dry casein are usually sufficient. Raschit is a para-chlorometacresol, and is used in amounts of 0.1 to 0.15%. Moldex, a para-hydroxy benzoate ester is very effective when used to the extent of 18 oz. per 100 gal. of glue.

In the following different casein glue compositions are given which were successful in actual practice or were recommended in the literature as really useful;

Plywood Glue

Casein	100kg
Water	350kg
Lime Hydrate	10kg
Sodium Silicate	15kg

Between the application of the glue on the plies and the pressing, 40 minutes to 2 hours should intervene. The best results were obtained when the temperature was 100°C., during the pressing, and the pressure is 14kg per sq. cm. The amount of glue used was 56g per sq. cm.

Casein Glue with Pine Oil Addition, Low Foaming

The addition of pine oil diminishes foaming during the solution of the powdered casein glue. For instance, one dissolves 100 parts of a mixture of

Casein	70kg
Trisodium Phosphate	10kg
Lime Hydrate	20kg
Sodium Fluoride	3kg

in 200 kg of water, containing two kg of pine oil.

Casein Glue for Furniture Factories, etc.

Lactic Acid Casein	50kg
Lime Hydrate	5kg
Chalk	10kg
Disodium Phosphate	5kg
Sodium Fluoride	5kg
Mineral Oil	2.5kg

This glue stays liquid for 6 to 8 hours, sticks well and only discolors very sensitive wood.

Simple Furniture Cold Glue

Casein	64kg
Lime Hydrate	23kg
Sodium Fluoride	9kg
Mineral Oil	4kg

Casein Cold Glue

Casein	50kg
Lime Hydrate	18kg
Trisodium Phosphate	7kg
Sodium Fluoride	3.3kg
Barium Sulphate	10kg
Mineral Oil	2kg

Veneer Cold Glue

Casein	69kg
Lime Hydrate	20kg
Sodium Fluoride	5kg
Sodium Sulphite	3kg
Mineral Oil	3kg

The fluoride and the sulphite give good brushability of the glue.

Furniture Cold Glue

Casein	65kg
Lime Hydrate	16kg
Trisodium Phosphate	5kg
Sodium Fluoride	4kg
Sodium Sulphite	5kg
Sodium Silicate, Powdered	3kg
Mineral Oil	2kg

Furniture Cold Glue

Casein	64.5kg
Lime Hydrate	6.5kg
Chalk	13kg
Disodium Phosphate	6.5kg
Sodium Fluoride	6.5kg
Mineral Oil	3kg

American Casein Glue

Casein	35kg
Sodium Hydroxide	2kg
Water	150kg
Benzine	110kg

Casein Cold Glue

Casein	30kg
Lime Hydrate	8kg
Trisodium Phosphate	3kg
Sodium Fluoride	1kg
Barium Sulphate	8kg

Barium sulphate is not desirable because it forms very hard glued joints.

Furniture Cold Glue

Casein	73kg
Lime Hydrate	20kg
Disodium Phosphate	5kg
Sodium Fluoride	3kg
Chalk	10kg
Mineral Oil	2.5kg

This glue stays liquid for 8 hours, sticks well, and hardly discolors sensitive woods.

Plywood Glue

In a large plywood factory, 50kg casein and 50kg blood albumen are used together with lime hydrate, made up with water in a mixture of 1 part of glue and 5.5 parts of water.

Casein Glue

Casein	70kg
Trisodium Phosphate	10kg
Lime Hydrate	20kg
Sodium Fluoride	3kg

Blood Albumen and Casein in Combination with Sodium Silicate

When blood albumen glues are used in the plywood industry for cold pressing (Conifera woods cannot be pressed hot), a definite alkali content is absolutely necessary. Therefore, according to U. S. Patent 1,976,346, the following is used:

Powdered Blood Albumen	100kg
Caustic Soda	8kg
Lime Hydrate	7kg
Sodium Silicate	30kg
Water	675-725kg

For blood albumen, casein or other vegetable proteins may be substituted. To glue plywood, use may be made of the moisture content of the wood. This is done by using blood albumen and sodium silicate which forms a water resistant glue film with the water of the wood when pressed. In this case the ratio of Na_2O: SiO_2 should not be smaller than 1:2. More detailed information is given in U. S patent 2,044,466. Another glue, also useful for the plywood industry and of

original composition is protected by U. S. Patent 2,016,707 for I. F. Laucks in Seattle. It requires

Casein	100.00kg
Sodium Fluoride	18.75kg
Zinc Oxide	1.25kg
China Clay	30.62kg
Bentonite	30.63kg
Lime Hydrate	43.75kg

This mixture is dissolved in 450kg of water.

Furniture Cold Glue

Casein	60kg
Lime Hydrate	20kg
Trisodium Phosphate	10kg
Sodium Sulphite	8kg
Mineral Oil	2kg

Use of Vegetable Proteins

According to U. S. Patent 1,962,808, the production of casein glues with low water content is possible, if "Isolated vegetable proteins" are added to the casein or are used by themselves. By these materials, proteins from the press-cake of soy bean oil and caster oil manufacture are meant. More detailed information* can be found under "Soy Bean Products in the Lacquer and Adhesive Industry" by Hadert, in the journal "Gelatine, Leim, Klebstoffe", No. 11/12, 1936, pg. 207-213. These proteins are obtained by extraction, solution in alkalies, and precipitation by acids. If one adds to a mixture of 300 parts of casein with 200 parts of protein a mixture of about 95 parts of lime hydrate with 74 parts of sodium fluoride, it is said that a valuable glue in powdered form for the wood industry can be obtained. The glue is dissolved in enough water to make it ready for application. Also ivory meal in finely ground form is claimed to be suitable as an addition to casein glues, as can be seen from the U. S. Patents 1,895,979, and 1,925,232. The addition of this meal makes the glue much thinner and after it has been added to the casein, a blood albumen solution is added as is usually done in the plywood industry.

* The latest book on this subject which treats with the subject of vegetable casein and its application is "The Soybean Industry - Horvath (Chem. Pub. Co. of N. Y.)

To make casein glues and such from proteins of soy beans and castor seeds water resistant, various waxes are used according to U. S. Patent 1,965,778. For instance, 1 part of wax is dissolved in 8 parts of carbon disulphide or carbon tetrachloride. Three parts of this solution are used for 100 parts of casein and 200 parts of water.

Another casein glue, using soy bean flour, consists of 50kg of casein, 50kg of trisodium phosphate or 100kg of soy bean flour, 20kg of barium hydroxide, 10kg of trisodium phosphate, and 17.5kg of lime hydrate. Blood albumen also is used in connection with trisodium phosphate, in the following composition: 52.5kg of blood albumen, 57.5kg of soy bean flour, 17kg of trisodium phosphate, and 15kg lime hydrate.

Although reports on soy bean proteins and glues made from them are more frequent in the last years, this application has been known for many years, namely from the now expired American Patents 1,275,308 (1918) and 1,321,480 (1919) for S. Satow. According to this procedure, the soy beans are dried at first, perhaps peeled, and extracted with naptha. The remaining soy bean flour is freed from the residual solvent by treating with hot air of 40°C. under stirring, or better in a vacuum. It is then treated with caustic soda or potash, ammonia or sodium carbonate solution. The extracted protein is separated by filtering, centrifuging, or by other physical or chemical methods. From the extract, the soy bean protein is precipitated by diluted sulphuric, phosphoric, acetic, lactic, or sulphurous acids. The supernatant liquid is drawn off and the precipitate which has settled out is pressed into cakes, dried, and pulverized. Such protein is said to be very valuable for adhesive manufacture.

A typical glue from soy bean protein consists of

Soy Bean Protein	100kg
Calcium Oxide	15kg
Water	500kg
Sodium Silicate	7kg
Cement	2kg

Calcium oxide, although dissolving the powdered glue faster than calcium hydroxide does, produces a powdered glue made with it to absorb moisture from the air very easily and to form lumps.

The use of sodium hydroxide, caustic soda, sodium carbonate etc. should be avoided in this formula since it considerably lowers the water resistance of the glue.

Even in the U. S. S. R., use has been made of the progress in production of soy bean glues. This is shown by the treatise in No. 9 of "Mechanical Wood Working", Moscow, 1936. There flour is obtained by grinding soy beans which are freed of oil and moisture. This is treated with caustic soda and thereafter with an acid (acetic, hydrochloric acid, etc.), yielding pure soy bean legumin. 100 parts of legumin are mixed with 700 to 800 parts of water, 20 parts of slaked lime, and 7-10 parts of sodium carbonate, which represents a glue. There is a consumption of dry adhesive of 27 grams per sq. m. for gluing. The glued wooden plates showed a resistance against splitting apart of 111-133 kg per sq. cm.

According to U. S. Patent 2,006,736, a glue can be made from soy beans by treating, for instance, 60 grams of soy beans with 100 grams of 10% caustic soda for 15 to 20 hours, and adding 80 grams of 55% phenol and 60 grams of a 40% carbohydrate. This is heated to 90°C. A clear, easily flowing glue is obtained. With Ivory Nut flour addition, the following glue is obtained:

Casein	60kg
Lime Hydrate	15kg
Trisodium Phosphate	4kg
Sodium Fluoride	4kg
Ivory Nut Flour	17kg

One part of water is stirred up with a half part of this mixture. After 20 minutes the glue becomes creamy.

More consideration is now being given to glues containing urea, about which we can say the following:

Urea has recently aroused great interest in the glue and adhesive industry (also for dextrin adhesives). Its use in this industry as a liquefier for glues is not new (German Patent 446,288 Bros. Merz & R. E. Liesegang, 1925). One can use, for instance, 200 grams of gelatin, 1kg of water, and 100 grams of urea. Also thiourea is used, as can be seen from U. S. Patent 1,394,654 by Donald K. Tressler. Thiourea has a stronger swelling action than urea, but is considerably more expensive. Urea has similar effects as the known glue liquefiers chloral hydrate, sodium alpha-

napthalene sulphonate etc. Urea is also found as softener for starch products, because urea as well as chloral hydrate favor swelling, whereas glucose and glycerin act against swelling in spite of their softening action. To dissolve casein, one uses, for instance, 100 kg of casein, 100-150 kg of water and 90kg of urea. Heating speeds up the action of the urea. Urea may be used together with sodium carbonate or ammonia, for instance as follows:

Casein	100kg
Sodium Carbonate	4kg
Urea	48kg
Water	160kg

or

Casein	60kg
Urea	16kg
Water	100kg
Ammonia (0.910)	2.5kg

It is an advantage to heat this, because, to keep a certain amount of animal glue liquid, one needs

20%	of	urea	at 18°C.	room	temperature
30%	"	"	" 14°C.	"	"
40%	"	"	" 10°C.	"	"
50%	"	"	" 7°C.	"	"

A special advantage is the use of urea to form glues which contain little water and much solids, since glues containing urea are thin even with little water.

A casein glue of

Lactic Acid Casein	100kg
Urea	100kg
Water	75kg

is stable for 2-4 days and is absolutely neutral. If latex is added to this mixture, an adhesive for "Cellophane" results (U. S. Patent 1,971,522). As an adhesive for "Cellophane" wraps for sausages, the following glue is given in U. S. Patent 1,962,763:

Rennet casein, 100kg, are soaked in an aqueous solution of urea. The aqueous solution is obtained by heating

the urea to 160-170°C. and dissolving 100 gram of this fused urea in 200 grams of water. By this heating, it is said that ureates containing cyanuric acid are formed.

Also ethanolamines which are good dissolving agents for neutral casein glues are used together with urea, according to the U. S. Patent 1,964,960 of the Perkins Glue Company. According to this patent, a wood glue is obtained by mixing one part of casein with less than 2 parts of ammonium sulphocyanate, urea and triethanolamine as well as 1.5-4 parts of water and with a small amount of paraformaldehyde. Special adhesives from casein are the following:

Adhesive Paste

A composition protected by British Patent 362,011 to R. Leibfarth, Metzingen, consists of 1kg of acid-free casein, 30 grams of borax, 55 grams of ammonium chloride in combination with albumen, sugar and sufficient water to form a homogeneous mass. Casein and borax are kneaded in the cold with part of the water and with the balance of the water at 70°C. To this, ammonium chloride, albumen, and sugar are added.

*Plastic Wood Type Dough in Collapsible Tubes
(Patented)

Casein	50kg
Lime Hydrate	8kg
Trisodium Phosphate	3kg
Sodium Fluoride	3kg
Mineral Oil	2kg
Hard Wood Flour	34kg

The mass is brought to tube consistency with water.

Adhesive to Paste Cork Plates etc. into Molded Bottle Tops

Glue Filler (Veltenia)	40-45kg
Yellow Dextrin	30-35kg
Casein	5-10kg
Fish Glue	3-6kg
Borax or Sodium Carbonate	1-3kg

Dextrin and Veltenia are mixed well and ground up to a paste with hot water, and are stored in air tight containers. The other raw materials are mixed separately and are

added to the paste shortly before use.

Label Glue for Tin Cans

Casein	1.00kg
Rosin, Finely Powdered	1.00kg
Borax	0.11kg

This mixture is made up with twice the amount of water.

Adhesive for Paper Bags for Coal, Concrete, etc.

Casein	100kg
Borax	16kg
Alum	11kg

This is dissolved in 4 to 5 times the above weight of water. The adhesive gives fairly water resistant gluings. A similar, but liquid glue consists of

Water	200.0kg
Casein	42.5kg
Borax	5.6kg
Phenol	8.1kg
Turpentine	0.1kg

The turpentine is added to cover the odor of the phenol.

Cement to Paste Galalith on Metal

Casein	5kg
Shellac	2kg
Borax	4kg

This should be made up with hot water.

Label Adhesive

1.	Casein	20kg
	Water	50kg
	Boric Acid	4kg
2.	Borax	4kg
	Water	5kg

Solution 2 is added with stirring at about 70°C. to solution 1. The mixture is allowed to stand one day. The foam

is removed. This is a gelatinous label adhesive of great stability.

Casein Putty for Application with a Spatula

Such a mass is used as a primer for paint coatings and has been found successful in the following composition:

Lithopone	100kg
Chalk	100kg
Casein Solution	50kg

The latter consisting of

Casein	100kg
Water	250kg
Caustic Potash	6kg
Borax	16kg

To make such a composition 100kg lithopone and 100kg chalk may also be bound up with 50kg of shellac soap. To make a casein-oil mass for the use with a spatula, 100kg of copal lacquer or synthetic resin (oil) lacquer are stirred up with a solution of 5kg of potassium hydroxide in 200kg of water. This emulsion is mixed hot with 400 to 500kg of the casein solution just mentioned and with 1000kg of lithopone and 1000kg of barium sulphate.

CHAPTER III

CASEIN PAINTS AND COLORS

Besides the oil paints, there are known water paints (glue paints) to paint walls, wooden objects, etc. These water paints are based on vegetable glues, animal glues and casein glues.

Water paints prepared with casein were particularly successful because they are very water resistant after their application and because they spread much more easily than a paint made from glutin glue. Casein glues have the further advantage that they can be made up as powders, mixed with pigments and filled into packages. The consumer only has to dissolve the powder in the prescribed amount of water to form a casein paint ready for use. Often, however, liquid casein paint binders or ready made casein paints in liquid form are sold (for instance sign paints). For use, the coloring ingredient (ochre, chromium yellow, etc.) is stirred into the binder, or if the paint is liquid, it is only diluted for application with brush or spray gun.

The various dissolving agents for casein have already been treated under Casein Glues. Borax, ammonia, and ammonium salts are successfully used for casein paint binders. Powdered casein paints often contain sodium carbonate and calcium oxide. Other dissolving agents usually have too high an alkalinity, causing the binders to decompose easily or the pigments to discolor. This is particularly evident in casein solutions made with borax which retain their viscosity and solutions with good viscosity. If some drying oil is added to such casein solutions (e.g. linseed oil or tunguoil), very stable casein emulsion paints of good brushability and water resistance are formed. To increase this water resistance further, for outdoor application, additions of marble lime hydrate, sodium silicate and so on, have been found valuable. For a cheap paint binder, casein may simply be dissolved in sodium silicate solution, to which soap suds are added, and preserved by phenol.

The normal casein paint binders in powdered form which do not have to give a water resistant coating, usually consist merely of casein and sodium bicarbonate; that is a mixture which forms a particularly light, loose and easily soluble powder because of the influence of the liberated carbon dioxide. Other commercial paint binders are simply mixtures of casein with sodium carbonate or with borax. One cannot ask much from such binders regarding their rub resistance. For lime paints, mixtures of casein, pigment, and lime hydrate are used. Exactly as in casein glues lime hydrate yields particularly water resistant films after drying. From other quarters we are informed, that besides borax and ammonia trisodium phosphate may be used as the dissolving agent. It has been found that the use of a liquid dissolving agent for casein gives better and glossier coatings than the use of powdered dissolving agents. Ammonia particularly acts very favorably in this respect. Triethanolamine has been found very successful, too. Of course, the grain size of the pigment used is of great importance in determining whether the coating is dull or of silky lustre.

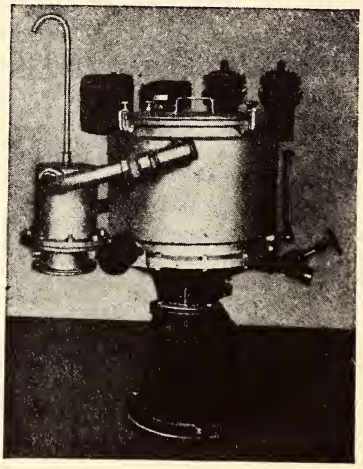
Many brands of casein are sold. Sometimes, the caseins are sold with an indication of their origin, namely as Argentinian, French, New Zealandic or German casein. Some are on the market under a trade name which guarantees controlled properties for all shipments which fact is very important for casein paints. For instance Dairyco Casein, Vencal Casein, Bomil Casein, Havero Casein, La Plata or Havero Casein La Blanca etc.

The marble lime hydrate used should be watched carefully for complete purity and the smallest possible magnesia content. Only air floated, very fine grades which are quick-acting should be used to produce powdered casein paints. Good lime hydrates contain 98% of calcium hydroxide.

The composition of casein paint binders corresponds approximately to the composition of a powdered or liquid casein glue becoming water resistant after drying with its various additions.

Phenols have been found valuable as preservatives. Their odor can be covered by the addition of a little turpentine or pine oil. A particularly freshly made lime hydrate should be used for powdered casein paints, even more so than in casein glues. It is made by slaking well

burnt lime with about 1/3 of water. It must be stored in air tight containers, and if possible the marble lime hydrate should be fine enough to pass through a German standard screen No. 30-40 (80-110 mesh per inch). Lime hydrate stored open in the air becomes useless because of the absorption of carbon dioxide and moisture from the air. Similarly as in casein glue, the ratio between lime hydrate and casein is important here. Too much of lime hydrate is not detrimental in outside paints, since the excess lime combines with the cement of the walls. In a discussion with one of the North American casein paint manufacturers, Mr. M. D. Swartz of the Farboil Paint Co. at Baltimore, he stated that the correct ratio of sulphuric acid casein to fresh lime hydrate is 100 : 87.5. This observation has been used repeatedly in the literature.



High Speed Gyro Dissolver and Mixer
with Temperature Control used for making
Casein Solutions

If the lime hydrate contains only 70% of calcium oxide, and 12kg of casein are used for 100kg of dry paint, 15kg of lime hydrate are necessary. If there is only 50% of calcium oxide in the hydrated lime, 21kg must be used. It is therefore, very important, when manufacturing casein paints, to try out exactly whether there is an excess of lime hydrate in the paint (for then the casein is bound too quickly and the paint is not rub resistant and cracks off).

If there is, on the other hand, too little of it the casein will dissolve incompletely and the paint will look chalky. Considering all this, a wall paint which is very successful today is produced as follows:

Casein	50.8kg
Ammonia 26° Be.	7.6liter
China Clay White, Finely Powdered	136kg
Whiting	136kg
Lithopone	204kg
Ultramarine Blue	0.7kg
Water	450liter
Hexamethylenetetramine	5.7kg

Other additions to casein paint binders are fillers, pigments free of gypsum, materials to prevent settling, to enhance the application by brush etc. The cheapest pigment of best hiding power, acting at the same time as filler, is whiting. Only the best whiting should be considered and should pass through a German standard screen No. 100. Precipitated calcium carbonate, although suggested for casein paints, has not been found valuable because of its low hiding power. Paints made with it do not have the consistency of paints made from natural whiting. Barium sulphate, asbestine, infusorial earth, magnesia, china clay and blanc fixe are used besides whiting. Colored pigments usually used are ochre, ultramarine blue, chromium yellow, chromium orange, zinc yellow, lime green, lime violet precipitated on green earth, lampblack, ivory black, bone black and other blacks, iron oxide, manganese brown and black, green chrome oxide and hydroxide, lithopone, zinc white, titanium white etc. China clay and asbestine are fillers rather than pigments. Titanium white, lithopone and zinc white have been found useful in emulsion binders and show their full effect in these rather than in pure casein binders.

Organic colors, such as Hansa Yellow, Lithol Red, Malachite Green, etc. are used, generally all lime resistant pigments. Mars colors, however, are poorly bound in outdoor paints.

To prevent the paints from running off the walls, about 2% of water soluble starch is added. The same result is sometimes obtained by the addition of china clay or asbestine. Bentonite grades recently produced in Germany have also been found useful. The brushability of the paint is enhanced by these additions, and the settling of the pig-

ments is retarded. The ratio of one part of casein to 1.2 parts of lime hydrate to five parts of pigment is mostly used. To make the finished coating wash resistant, the addition of lime hydrate is usually enough, but may be enhanced by formaldehyde or hexamethylenetetramine as shown in the previously mentioned American formula. About 5 to 8% of hexamethylenetetramine, on the basis of the casein, makes the paint insoluble. The latter, however, is expensive; formaldehyde, on the other hand, should be used with caution because it thickens the paint too quickly. Therefore, lime hydrate is still the best addition to create water resistance. Recently, acetaldehyde and furfurol have been suggested as additions to increase water resistance. The latter, however, retards the thickening of lime containing casein paints.

When testing for water resistance and rub resistance it should be considered that not all pigments give water resistant paints with the same binder. Whereas, for instance ochre is easily bound water resistant by casein, ultramarine pigments are much more difficult to bind this way. Coatings which peel off easily can be improved by the addition of Turkey red oil. This oil is also added to such paints which are applied in the neighborhood of stoves or to paints to be used in the tropics.

The covering power of casein paints is also very important. Generally it is figured that 1kg ordinary oil free casein paint can be spread over 5-15 sq. meters. Good hiding paints, particularly paints containing lithopone, zinc white or titanium white allow a spreading over 8-10 sq. m. surface. If, therefore, a good yield is desired with colored pigments, it is always good to use one of these white pigments together with the colored one, since this has a much better action than the cheap chalk.

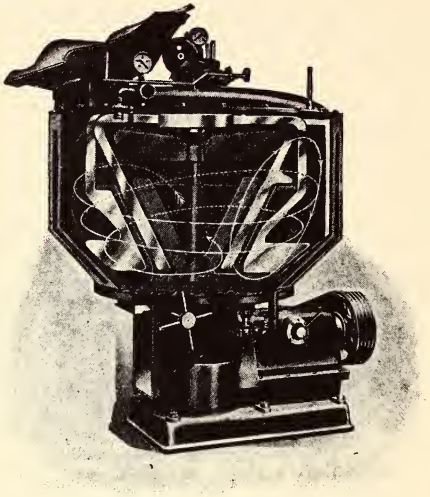
Corrosive mercury sublimate is often used as a preservative. One kg of it is usually used on 1000kg of whiting. Of this mixture, 3/4% is added to the finished paint. This addition prevents mold growth on the walls, attack by insects etc. It cannot be recommended to use zinc sulphate which is given in an American formula quoted below, since it forms a coating which cracks off easily. A Raschit emulsion, liquid or powdered, is easily water soluble and has been found suitable. Casein solutions with lime, zinc white or borax can be stored without preservative without showing mold growth.

The use of phenolic resins in casein emulsion binders or of Beckosols (containing at the same time certain amounts of oil) also make unnecessary the use of a preservative. Such paints are protected, even on the wall, against decomposition and insect attack. It is not advisable to use beta naphthol, salicylic acid, or cresol as preservatives. The latter two often cause discoloration in light paints. The use of pine oil, 50 grams per 1kg of casein paint is recommended as a mold preservative. At the same time a paint containing it flows better and therefore permits covering a larger area with the same amount of paint.

Water casein paints are not the only ones known. There are such paints to which oils, waxes, latex, resins etc. are added. Casein emulsion paints containing oils or resins give lustrous coatings. As oil linseed oil or tung oil is usually taken, either raw or boiled oil. Emulsion binders made with boiled oil dry well and thoroughly and should therefore be preferred. Usually one part of linseed oil stand oil is mixed with one part of linseed oil varnish.

Since oils containing casein paints (particularly those without stand oil) tend to settle out their pigments, it is advisable to prevent the sedimentation or separation of the paint mixture by adding Turkey red oil or wax emulsions. If latex is added, the dried film becomes particularly elastic and stable against moisture. Therefore, such mixtures are used for street marking paints which must possess a great resistance to wear.

Where casein binders are to be emulsified with linseed oil varnish, trisodium phosphate has been successfully used. If ammonia, sodium carbonate, caustic potash, etc. are used, they easily cause thickening when the casein solution is mixed with the varnish. From various sides, however, strong alkalies have been recommended. Such a difference of opinion often occurs, particularly in the casein glue or paint field. In the production of a casein solution it is best to soak the casein in hot water, to add alkali at about 60°C., and to cool down to 40°C. before adding the oils or resin solutions. As siccatives (driers) for oil containing casein paints, cobalt linoleate, manganese borate, or lead oxide are used. In connection with the production of casein paints it should be mentioned, that powdered casein paints are made up in exactly the same mixers as the powdered casein glues. For casein paints or casein paint binders containing oils or in paste form, gyro-mixers have been



Cross Section of Gyro Dissolver

found excellent. Turbo-mixers, too, are often used to make up emulsion binders. Mixed powdered paints must be ground once again, if they show lump formation, and are then packed into packages which are air tight. Powdered casein paints must be mixed particularly well lest an inhomogeneous finished paint is formed because of carelessness in dissolving the paints in water. Such a paint gives streaky walls.

It can easily be determined, whether the composition of a casein paint is correct, by simply spreading some of the finished paint on parchment. If after the drying on the parchment the paint cracks off when the parchment is rolled or folded, the paint contains too little casein. The paint contains too much casein if it causes paper for artistic printing, on which it has been spread, to wrinkle. One cannot expect that these coatings will show the desired water resistance immediately after their application. These paints require about 2 to 3 days drying after application, before they will stand washing off. The paint may also be brushed on parchment, and the film may be put under a shower for some hours. If it can stand this test it can be called water resistant.

The following have been successfully used by me and others in commercial practice. Small changes will be necessary in the adaptation of these formulae because of the differences in the raw materials.

Powdered Casein Paint

Casein	10kg
Lime Hydrate	10kg
Pigment	50-80kg

If the paint is intended for outdoor coatings, the lime hydrate has to be increased to a ratio of 5 parts of lime hydrate to about 2 parts of casein.

Dull Casein Cold Paint

A water resistant paint of good hiding power consists of

Casein	10kg
Lime Hydrate	10kg
Clay, Finely Powdered	10kg
Pigment	10kg
Chalk	60kg

The addition of clay prevents the settling of the solids, while the chalk gives good hiding power. In addition, the clay permits easy spreading. To prevent the settling, addition of dextrin is recommended. However, the water resistance of the paint suffers considerably from this addition, because dextrin containing paints easily absorb water. Special water resistance can be obtained if a small amount of 2% formaldehyde is added to the water in which the casein paint is dissolved.

Casein Sign Paints

This type sign paint is not quite as water resistant and weather resistant as those made with resin varnishes. As dissolving agents for the casein ammonia, ammonium bicarbonate, or trisodium phosphate are particularly suitable. Commercial caseins for technical purposes have acid values of 12-20. There are especially purified grades of an acid value of only about 0.3 to 0.7. Pure (neutral) casein requires 2.8% of sodium hydroxide, that is 2.8 weight parts of anhydrous, pure sodium hydroxide per hundred weight parts of casein. Accordingly, 100 grams of casein of an acid value of 14.5 can be dissolved by 6 grams of potassium hydroxide or by 6 grams of ammonia (0.895) and 250 grams of water. The reaction of these three raw materials takes place with stirring on the water bath. The solution is diluted for use as a paint binder with 250 grams more of water. A casein solution made with trisodium phosphate can be made from 10kg of casein which is gently heated with 30kg of water. To this a solution consisting of 1.1 kg of caustic soda in 3 kg of water is added. The finished mixture is diluted with an additional 30kg of water before use. If the paints are intended to be glossy, one can work with an emulsion paint, or additions of shellac, Beckosol, Alkydal, etc. may be made. Pigments for sign colors must be light and lime resistant. The finished paints must contain a good preservative.

Lacquer for Wood Coating

The following solution is used as a transparent coating solution for wood and especially for paper. 100 grams of casein, completely free of fat and essentially free of ash, is soaked in 100 grams of water for 3 hours. 60cc of concentrated aqua ammonia is added, and this mixture is heated on a water bath with stirring, until a paste free of lumps is formed. The mixture is diluted with 1.5 liters of

water. It is filtered clear through asbestos fibre and mixed with a formaldehyde solution of about 40% strength. Enough formaldehyde is added to make its odor noticeable in the mixture.

Normal Commercial Casein Paint

Casein	12kg
Lime Hydrate	15kg
Trisodium Phosphate	1kg
Whiting	55kg
China Clay or Infusorial Earth	15kg
Dextrin	2kg
Preservative	0.1kg

If the finished mixture is too thick, its fluidity may be improved by adding a little sodium fluoride.

Other casein paint binders are: 100kg of casein is kneaded with 15kg of ammonia, 25%, and 15-18kg of concentrated sodium carbonate solution. 100kg of casein may also be dissolved by 10kg of borax and 5kg of ammonia (0.910) in hot water. Both materials are to be diluted with water to the desired concentration.

It should never be overlooked, in the production of oil emulsion paints, that too large an oil content makes paints, and particularly the light ones, appear yellow. A casein paint to which turpentine has been added and which, therefore, has its resin and oil content partly dissolved, consists, for example, of 30kg of casein, 150kg of water, 3.5kg of borax, and 1kg of preservative. This solution is allowed to stand for 24 hrs. To this, 2kg of formaldehyde are added in 5kg of water. After stirring up well, 15kg of rosin, 15kg of boiled linseed oil, and 10kg of white spirit are added. Pigments are added as desired, using 6-8 times the weight of the binder. Other compositions are:

Linseed Oil	9kg
Water	16kg
Alum	1kg
Casein	4kg
Preservative	0.1kg
Wetting Agent*	0.1kg

*Alkanol B. Sulfatate, Wetanol or other good wetting agents.

Or

Potato Starch	10kg
Water	30kg
Casein	6kg
Linseed Oil Varnish	80kg
Water	170kg
Ammonium Oleate	3kg

Or

Casein	3kg
Water	30kg
Borax	0.35kg
Phenol	0.2kg
Formaldehyde	0.2kg
Resin	1.5kg
Linseed Oil	1.5kg
White Spirit	2kg
Emulphor FM (or other Emulsifying agent)	0.2kg

It is also possible to form an emulsion from 65% of oil, 30% of ammonia, 5% of soap in a turbo mixer and to add 1 or 2% of this to a pure casein paint.

To combine casein in a suitable way with linseed oil, casein is dissolved hot in a little water containing borax or trisodium phosphate, yielding a paste. Then a finely powdered rosin or rosin soap is added and this mixture is stirred into the oil. It is best to use the turbo-mixer for this since it finishes the process in a few minutes. If trisodium phosphate is used, addition of a little sodium carbonate is favorable to guarantee a better stability of the emulsion.

Tin Can Paint

Oil Emulsion with Animal Glue	7kg
Casein	1kg
Ammonia	1kg
Nitrobenzol	0.1kg
Estolan HM37	0.05kg

Paint for Spinnery Spools

100 grams of casein are dissolved in 500 grams of water by means of 24 grams of caustic soda. The solution is heated to 70°C. and stirred well. To this solution, 100

grams of the primary condensation product of phenol and formaldehyde are added. Such a product may be obtained by heating 130 grams of phenol with 130 grams of a 30% formaldehyde solution and 8.5 grams of caustic soda. 22% of ester gum, 56% of linseed oil, and 32% of turpentine are added to this mixture. With such a composition big spinneries protect their spools against the influence of moisture. It is better to buy a finished phenol formaldehyde synthetic resin to prevent difficulties (Bakelite Beckacite, etc.)

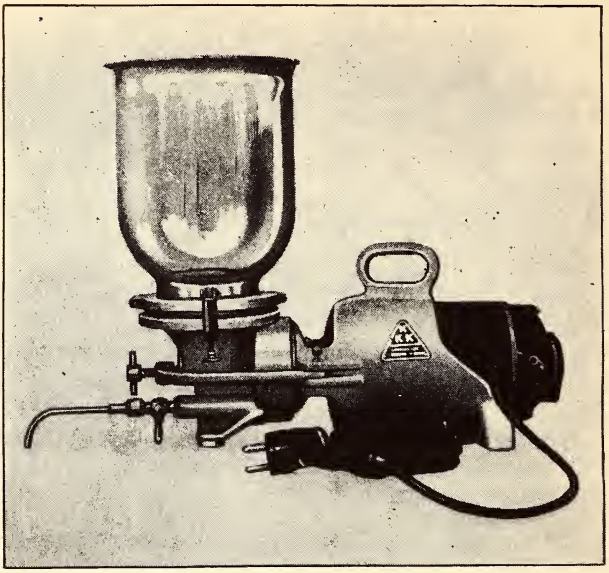
Lacquer for Emulsion Paints

Emulsion paints may also be made up by simply mixing a lacquer with a casein solution. Such a lacquer which is easy to mix and does not show any separation in the finished mixture, consists of 1 part of Manila copal and 2-2.5 parts of linseed oil with about 0.75 parts of stand oil and 0.75 parts of slightly thickened tung oil. Everything is mixed well and the finished lacquer is added into the casein solution with stirring. Casein solution and oil (particularly if the latter prevails) are easily emulsified by vigorous stirring. The formation of an emulsion is favored by the use of turbo-mixers and the addition of emulsifiers, as for instance ammonium linoleate. If ammonium linoleate is used, it is possible without difficulty to add pine oil to the paint. Thus 60 parts of pine oil may for instance be compounded with 7 parts of ammonium linoleate and 60 parts of water without any difficulty. In the turbo-mixer, such an emulsion forms in a few minutes.

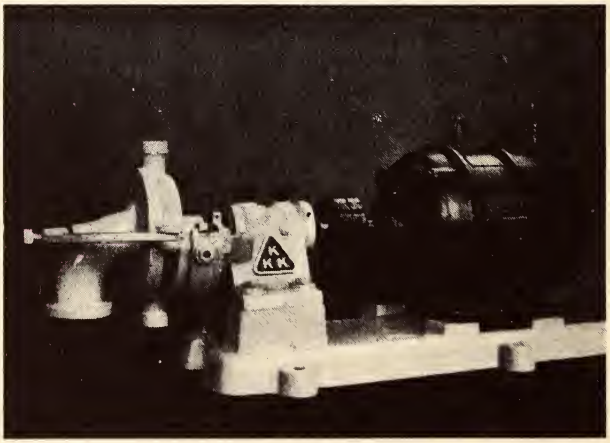
Of course, there are numerous other methods of production, some of which are patented. In these cases gelatin, latex, shellac, etc. are combined with casein yielding a casein emulsion for certain industrial purposes. Very detailed information and numerous suggestions are given in the U. S. Patents No. 1,604,307 to 1,604,317, about the manufacture of casein solutions. These formulas are given below:

1. Casein 50-70 parts; Calcium Hydroxide 10-20 parts; Sodium Fluoride 1-12 parts; Trisodium Phosphate 1-15 parts; Calcium Chloride 1-7 parts; Hydrocarbons 1-4 parts; Citronella Oil 1-4 parts.

2. Casein 50-75 parts; Calcium Hydroxide 6-20 parts; Trisodium Phosphate 4-12 parts; Sodium Sulphate 3-8 parts;



Small Laboratory Turbomixer (KKK System)



Production Turbomixer (KKK System)

Sodium Hydroxide 2-10 parts.

3. Casein 50-75 parts; Cassava Starch 3-20 parts; Sodium Fluoride 1-10 parts; Trisodium Phosphate 3-15 parts; Calcium Chloride 1-6 parts; Calcium Oxide 4-12 parts; Magnesium Oxide 10-20 parts; Oil 1-4 parts.

4. Casein 50-75 parts; Calcium Hydroxide 10-30 parts; Calcium Tannate 2-8 parts; Sodium Fluoride 2-8 parts; Sodium Phosphate 3-15 parts; Calcium Chloride 4-10 parts.

5. Casein 50-75 parts; Potassium Aluminate 3-12 parts; Potassium Ferrocyanide 1-4 parts; Calcium Oxide 10-30 parts; Sodium Hydroxide 3-12 parts; Sodium Silicate 1-15 parts.

6. Casein 50-75 parts; Dextrin 5-20 parts; Sodium Aluminate 3-15 parts; Calcium Tannate 2-8 parts; Sodium Fluoride 3-10 parts; Calcium Chloride 2-6 parts; Sodium Formate $\frac{1}{2}$-3 parts.

7. Casein 50-75 parts; Sodium Silicate 2-10 parts; Trisodium Phosphate 3-15 parts; Sodium Sulphite 3-18 parts; Calcium Oxide 6-15 parts; Magnesium Oxide 10-25 parts.

8. Casein 50-75 parts; Calcium Hydroxide 8-10 parts; Magnesium Oxide 10-20 parts; Sodium Sulphate 3-10 parts; Arsenic 0-5 parts; Hydrocarbons 3-6 parts; Rosin 1-4 parts.

9. Casein 50-75 parts; Calcium Hydroxide 10-30 parts; Sodium Sulphite 3-10 parts; Trisodium Phosphate 10-20 parts; Sodium Molybdate $\frac{1}{2}$-4 parts; Calcium Chloride 5-15 parts.

10. Casein 50-75 parts; Calcium Hydroxide 10-22 parts; Sodium Fluoride 2-10 parts; Sodium Sulphite 3-8 parts; Magnesium Oxide 5-14 parts; Zinc Oxide 1-4 parts; Sodium Formate $\frac{1}{2}$-3 parts; Kerosene 3-5 parts.

11. Casein 50-75 parts; Calcium Hydroxide 10-30 parts; Trisodium Phosphate 5-20 parts; Sodium Fluoride 2-12 parts; Sodium Silicate 3-18 parts; Copper Chloride 1-5 parts; Sodium Formate $\frac{1}{2}$-3 parts.

Wherever sodium silicate appears in these formulas, sodium metasilicate should be used when transforming them into paint binders; this offers the advantage over borax in forming an insoluble product with lime.

German Patent 345,684 covers the use of barium superoxide to form water resistant casein solutions. German Patent 424,745 specified the use of aluminum sulphate for making casein solutions water resistant. German Patent 548,395 covers the addition of materials containing alkyl-, cycloalkyl-, or aralkyl- groups as emulsifiers in casein solutions. German Patent 270,200 shows how free rosin acids are brought into a colloidal solution in casein solutions by means of alkali. As German Patent 406,401 shows, casein solutions are made insoluble after drying by the addition of powdered sulphur. The use of magnesium oxide is protected by German Patent 542,442. There are many other and similar additions which mean to represent one or another change, but practical applications of these are very limited.

There are no standard specifications for casein paints in Germany as yet.

The following are official specifications of the American Army and Navy:

Cold water paints should consist of a homogeneous mixture of whiting, unreacted lime, and casein together with zinc sulphate as a protecting agent. The free calcium hydroxide content should be between 5 and 10%. The casein content should be between 10 and 12% (calculation: nitrogen x 8.1). There should not be more than 1.5% of silicic acid and silicates. If the material is dissolved in cold water, it should be possible to mix it smoothly after 15 hours and it should not exhibit any bad odor. The finished paint should dry pure white and should not dissolve on washing with cold water. The merchandise must correspond exactly to the standard sample furnished by the navy yard. The army specifications contain in addition a paragraph according to which the powdered paint should mix well also with hot water and should not exhibit bad odor after standing for 72 hours at room temperature. The paint should flow easily and should give good hiding in a single coating.

English Casein Emulsion Binder

Soak 10kg of casein in 25kg of water. Add 0.6kg of potassium hydroxide in 2kg of water with good stirring. Heat to 75°C. with continued stirring, cool, add 4 to 5kg of linseed oil varnish and mix thoroughly in a gyromixer or in a colloid mill.

American Casein Paint Binder

American casein suppliers have been recommending the following for some time:

I. The following mixtures are prepared separately

1.	Potato Starch	10kg
	Water	30kg
	Caustic Soda (10°Bé)	10kg
2.	Casein	6kg
	Water	20kg
	Caustic Soda (10°Bé)	10kg
3.	Water	150kg
	Linseed Oil Varnish	80kg

These three mixtures can be stirred together into a smooth emulsion which will remain stable for 6-8 months.

II. The paint may also be made up as follows, being especially suitable for coatings strongly exposed to wear:

1.	Casein	30kg
	Water	150kg
	Borax	3.5kg
	Phenol	1kg
2.	Formaldehyde (40%)	2kg
	Water	5kg
3.	Rosin	15kg
	Linseed Oil Varnish	15kg
	White Spirit	10kg

The casein is soaked in hot water, and the borax and later the phenol are added. After standing for 24 hours, the ingredients of group 2 are mixed in, followed by the ingredients of group 3 which had been mixed hot previously. Since the pigments are more easily wetted in oil than in water, it is advisable to grind them with the oil binder 3, before this is emulsified with the casein solution. The amount of pigment averages about 6 to 8 times the amount of the binder. Casein paints thus made excel by their good brushability and increased water resistance.

The following formulas of casein paints, taken from the literature, were made up experimentally and were found to various defects.

Casein	12kg
Lime Hydrate	15kg
Zinc White	5kg
Chalk	67.5kg
Phenol	0.5kg

Or

Casein	15kg
Lime Hydrate	17kg
Borax	6.3kg
Chalk	64.5kg
Phenol	0.5kg

Or

Casein	12kg
Lime	15kg
Trisodium Phosphate	1kg
Clay	15kg
Chalk	55kg
Preservative	0.25kg

These paints, particularly the white ones, possess poor hiding power. When the dried coatings are moistened with water, a "bronze" deposit is formed which is particularly noticeable on white paints containing chalk and on colored ones containing chrome orange. Dark paints such as gray or brown, show whitish stains besides the aforementioned deposit. These phenomena were investigated on 36 paints made up according to the two following formulas:

	I	II
Casein	12	12
Lime Hydrate	2-20	2-20
Borax	0.5	0.5
Chalk	85.5-86.75	80-62
Chrome Orange		5
Phenol	0.5	0.5

By using 2 and 3% as well as 4% of lime, these defects could not be observed, neither in the white nor in the colored coating. They show up, however, when the lime content is stepped up further. At the same time, the amount of lime hydrate necessary to dissolve the casein was found to be 2% of the total weight, respectively 16.6% on the basis of the casein used. Experiments on the stability of solutions with different lime contents, though still requir-

ing a control experiment, show that poor results are given by 12.5% lime on the basis of the casein, as given in many formulas. The coatings were tested for their stability on wood and walls. Thus coatings were made on wooden boards previously cleansed with sand paper, applying twice, paints of varying lime content in certain intervals of time. They were tested for their stability after 18, 36, 80 hours and after 18 days. The testing method consisted in rubbing the surfaces with a hard moistened brush. Paints with 3% of lime were the most stable, in some cases such with 4 and 7% calculated on the total paint. A casein content between 3 and 15% was always correct. The paint is not very stable with 3% of casein, but with more casein the stability increases up to 15% casein.

French Casein Paints

30kg lime hydrate, 35kg casein, and 10kg potassium silicate are stirred up with 500kg of water, heated up slightly and mixed with chalk and pigment.

200kg casein, 100kg chalk, 40kg borax, 500kg lead white or zinc white.

500kg casein, 30kg ammonia, 2000kg chalk, 10kg water. To this mixture 10kg of formaldehyde is added as soon as the casein is dissolved. This formula cannot be correct because of the small water content.

3kg of casein, 2kg of ammonia, 30kg of boiling water and 50kg of Portland cement. This mixture gives very stable paints, but must be applied immediately after being made.

100kg of chalk, 100kg of casein, 4kg of borax, and 400kg of pigments.

7kg of casein, 20kg of lime hydrate, 100kg of barium sulphate, 8kg of dextrin and 8kg of soap.

9kg of casein, 5kg of sodium carbonate and 6kg of lime hydrate.

12kg of casein, 7kg of sodium carbonate, 20kg of barium sulphate, 15kg of chromium yellow and 46kg of chalk.

English Casein-Oil Emulsion Paint Binders

Water	20kg
Potato Starch	10kg
Water	30kg
Lactic Acid Casein	6kg
Caustic Soda, (10°Bé)	10kg
Easter Gum	20kg
Linseed Oil	50kg
Lacquer Benzine	30kg
Manganese Resinate	0.1kg
Water	180kg

Or

Casein	120kg
Water	600kg
Borax	24kg
Ammonia	3kg
Potassium Bichromate Solution, (10%)	30kg
Nitrobenzene	3kg
Linseed Oil Varnish	45kg
Rosin	45kg
Lacquer Benzine	25kg

Or

Sodium Silicate	5kg
Water	45kg
Linseed Oil Stand Oil with Drier	50kg
Pigment	50kg

Or

Linseed Oil	9kg
Water	16kg
Alum	1kg
Animal Glue	4kg
Preventol	0.1kg
Wetting Agent	0.1kg

Or

Casein	3kg
Water	30kg
Borax	35kg
Phenol	0.2kg
Formaldehyde	0.2kg
Rosin	1.5kg
Linseed Oil, Bleached, Boiled	1.5kg
Benzine	2kg
Emulphor FM (Emulsifying Agent)	0.2kg

Or

Casein	80kg
Borax	12kg
Water	480kg
Ammonia, 0.880	3.25kg
Phenol Solution, Saturated	0.75kg

Of this casein solution 3.3kg are used together with 4.2kg of water and 22.5kg of lithopone to make a second solution. This finished paint then consists of 14kg of the first solution, 32kg of the second solution to which 16kg of latex were added.

Or

Latex, 60%	4.5kg
Casein	0.226kg
Preservative	14.2cc
to be stirred into	
Pigment	1.8kg
Water	0.9kg
Linseed Oil	0.12kg
Emulsifying Agent	7cc

Casein Paint Binder, pH below 7

Australian Patent 20,249, the Muralo Co. Inc. covers a method to make casein solution with low pH values. 100kg of hydrochloric acid casein are mixed with 15kg of sodium fluoride and heated to 76-99°C. This is finally diluted with water. This solution has a pH value of 6.1 and can be diluted with borax or ammonium carbonate. To obtain an alkaline reaction, organic basis may be added, such as diethylamine, ethylamine, hydroxyethylamine, ethylene diamine. For instance the following mixture is used: 100kg of casein, 150kg of water, 14kg of sodium fluoride, 5kg of ammonium fluoride, and 7kg of powdered quartz. This mixture is heated to 90.5°C. and is kept at that temperature for 0.5 to 1 hour. This solution is cooled to 49°C. and a further 300kg of water is added. The finished solution has a pH value of 6.9 to 7. Such solutions may also be mixed with synthetic resins, as for instance with ammonium glycerol phthalate resins (Ellisol B), and with softeners, such as Cellosolve, pine oil and Hexalin.

Casein-Oil-Emulsion Binder

Casein	10kg
Borax	1.5kg
Water	40kg
Linseed Oil Stand Oil	2.5kg
Cobalt Linoleate	0.05kg
Formaldehyde	0.200kg
Phenol	0.300kg

The latter two materials are added as preservatives and to increase the water resistance, Pigments are added to this binder as desired.

White English Casein-Oil Emulsion Paint

Lithopone	136.1kg
Barium Sulphate	13.6kg
Zinc Oxide	11.3kg
Chalk	4.5kg
Casein	4.5kg
Borax	0.45kg
Lanolin or Petrolatum	6.8kg
Boiled Drying Oil	15.9kg
Soap	2.3kg
Water	272.2kg

Colored English Oil Bound Water Paint

Whiting	136.1kg
Lithopone	13.6kg
Colored Pigment	9.1kg
Animal Glue	3.6kg
Casein	1.8kg
Borax	0.11kg
Oil Varnish	13.6kg
Soap	1.4kg
Cresol	0.23kg
Water	45.4kg

Glue Paint Binder

German Patent 605,484 describes a paint binder also suitable for use on top of old oil paint, consisting of 100 parts of casein, 300 parts of water, 100 parts of linseed oil varnish, and 150 parts of concentrated ammonia.

Casein Paint Binder for the Manufacture of Colored Papers

This is a viscous casein glue consisting of

Casein	20kg
Water	80kg
Borax	3kg
Ammonia, (0.900)	2kg

This glue is thinned with water until brushable. A thin glue is obtained from

Casein	5kg
Water	25kg
Ammonia, (0.900)	2.5kg

Both glues were found successful as paint binders in the colored paper industry.

Street Marking Paint (Traffic Line Paint)

Casein	20kg
Lime Hydrate	100kg
Trisodium Phosphate	12kg
Chalk	30kg

This mixture must be stirred into water where it is to be used, and must be used soon. It is better to add ester gum to such marking paints.

Printing Ink Binder for Paper Napkins

Water	5kg
Borax	0.3kg
Ammonia	0.1kg
Shellac	0.75kg

These materials are brought into solution. 1.5kg of casein is added, which previously was soaked over night with 4kg of water. This viscous binder is mixed with pigment as desired. The binder is also suitable for aluminum and gold bronze printing after being mixed with the proper pigment.

Printing Ink Binder for Pure Bronze Printing

A binder for paper printing especially compounded for bronze work consists of

Casein	10kg
Water	40kg
Borax	0.5kg
Ammonium Carbonate	0.5kg

C H A P T E R IV

OTHER APPLICATIONS OF CASEIN

Compositions similar to those of the casein glues and of the casein paint binders find application in numerous other branches of industry.

In the manufacture of paper for artistic printing, large amounts of casein are used. In Germany, 3000 tons of casein are estimated to be used annually in the paper industry. It is, however, being discussed whether casein can be replaced advantageously by other glues in the sized paper industry. This is denied by Fritz Hoyer in a longer article in the journal "Gelatine, Leim, Klebstoffe", No. 9/10, pg. 174-176, 1935. In the paper industry, the casein is soaked in water, mostly with heating. This led to the interesting observation, that a glassy and sticky as well as lumpy mass is obtained with water of 80°C. Such a mass will offer difficulty to solution by the addition of alkali. If the casein is soaked in cold water at first and then is heated to 80°C., this phenomenon is not observed. In the paper industry no potassium salts are used as alkalies because of their cost. Sodium carbonate, sodium phosphate, caustic soda, borax, and ammonia are used instead. Particularly ammonia is used where the highest possible water resistance of the papers is desired, and also where the paper surface should have as little alkalinity as possible. Lime Hydrate is not favored as a dissolving agent for casein since the size solutions for the paper solidify too quickly and because its use easily leads to foaming which must be avoided by all means in the paper industry. It is characteristic, that in the paper industry the alkalies required for the solution of the casein are mostly used in mixtures. To dissolve 100kg of casein the following amounts of alkali are used approximately in the paper industry:

3.15kg ammonium hydroxide, or
3.95kg sodium hydroxide, or
5.14kg sodium carbonate, calcined, or

12.30kg trisodium phosphate, or
14kg sodium sulphite, or
14.7kg borax

According to Clark in his book "Manufacture of Pulp and Paper", the following casein glues have been successful for coating papers.

	1	2	3	4
	kg	kg	kg	kg
Casein	100	100	100	100
Borax	5	4.5	3.2	5.5
Trisodium Phosphate	6.4	29.6	20.8	7.4
Sodium Carbonate		5.5		
Ammonia, 0.900	15	3	3	3

After the glues are made up, they are filled with various materials. To bind about 100kg of blanc fixe, about 6-7kg of casein are needed. For 100kg of precipitated calcium carbonate one needs about 8-10kg of casein, to bind 100kg of China clay, about 7-11kg of casein, and about 12-16kg of casein are needed to bind 100kg of satin white. Details of the use of casein in the coated paper industry are given in an article by G Leschanowsky, in "Gelatine, Leim, Klebstoffe", No. 7, pg. 126-130, 1933.

The application of these paper sizes takes place in the coating machines, which will coat 50-100cm of paper per minute. The only preservative for such brushing mixture which does not discolor the paper is borax. One can also use camphor and some essential oils. Even these coating mixtures are usually perfumed to cover the clearly perceptible cheese odor noticed in the summer on such papers. The waterproofing of coated papers takes place after the coating is made. This is done by forming metal caseinates with solutions of chromium alum, copper sulphate, iron chloride, lead acetate, etc. on the paper. The chief hardening agent used however, is the formaldehyde.

Another field for the use of casein is in the production of synthetic resins such as Galalith. The production of these masses is based on a hardening process brought about by the reaction of casein with formaldehyde. The formaldehyde solutions must be used very weak to prevent too

strong a surface hardening, and also not to hinder the penetration of the formaldehyde solutions or vapors into the interior of the casein layer. The most favorable concentration of formaldehyde is between 6 and 10%. The best pH value for this hardening process is about 5.5 to 6. The swelling of the casein masses is slight at a pH value of 4.6 and, also, the penetration is only poor. With the increase of this value, the penetration is increased and discoloration is observed. Fractioning was observed at a value of 2.5 and above 4.7. The temperature during the hardening is about 18-20°C. Below 15°C., penetration is retarded, and at higher temperatures the casein will swell excessively. Certain salts will favor this process, others retard it. Among the former are sulphocyanides, chlorides, carbonates, phosphates, borates, salicylates, tartrates, sulphites, and fluorides of alkali metals. Very satisfactory are sodium sulphocyanide and fluoride. On the other hand, alum, ammonium bicarbonate, zinc chloride, sodium acetate and sulphate will act as retardants.

The gel-like casein masses are molded into the many different shapes, such as boxes, combs, etc. and are hardened afterwards. For the casein resin industry, rennet casein is favored because it gives harder resins and is penetrated better by coloring matter. There is a longer article on casein in the artificial resin industry by K. Haupt in "Gelatine, Leim, Klebstoffe", February issue 1934, p.37 and in the same journal, No. 1 p. 9, 1933. Casein synthetic resin (artificial horn) is furnished in plates, tubes and rods. The hardening process, proper, takes days or weeks, depending on the method and the size of the articles made. From this resin, buttons, buckles, penholders, bracelets and tooth-brush handles are cut or turned. In general, the use of this artificial horn is continuously increasing.

By pressing casein solutions into woods with subsequent hardening, hard woods are made as substitutes for expensive natural woods.

Casein is also used to make corks from artificial cork discs. For this, casein is dissolved in water by borax and sodium phosphate, and glycerin is added. Cork waste is stirred into this mixture which is then molded into corks or cork discs.

Casein is also used in large amounts in the leather industry. An excellent article which also gives the important requirements for the casein, was written by Anton Hevesi in "Gelatine, Leim, Klebstoffe", No. 3/4, p. 43-48, 1935. Casein is also used for the degumming and the discolorizing of fibres. 80 grams of sodium carbonate are dissolved in hot water, and 80 grams of rosin and 250-300 grams casein are added (British Patent 424,189).

The chemical factory von Heyden at Radebeul makes a substitute for ivory from casein and sodium hydroxide. Casein is also used for the manufacture of printing inks giving water paint like colors.

Numerous textile finishes, putties, and special adhesives are made from casein. It is also used in medicine and in the manufacture of food products. A textile fibre, (Lanital) is now being made from casein.

Lanital fibre resembles a highly damaged wool in physical and chemical properties. It is more resistant to alkalies and less resistant to acids. It has a low wet strength. Accordingly it is used in admixture with wool and other fibres.

MISCELLANEOUS FORMULAE USING CASEIN

Flexible Printing Roller Composition

Casein Glue Solution	10 lb.
Glycerin	5 lb.
Molasses	5 lb.
Clove Oil	1 oz.

Mix until uniform and pour into molds.

Chrome Tan Calf Leather Finish

Gelatin	1 1/2 oz.
Casein	1 1/2 oz.
Borax	3/4 oz.
Shellac	2 oz.
Dextrin	3 oz.
Water to make	1 gal.
Pigment to suit	

Leather Finish

Casein, Lactic	2 lb.
Borax	5 1/2 oz.
Water	9 lb.
Milk	10 oz.

Add casein in water and milk heated to 130°F. Add borax while stirring. Add less than 10% very cold formaldehyde, after cooling, in a thin stream, with stirring.

Radiator Stop Leak
(Patented)

Flaxseed, Ground	16 2/3 oz.
Aluminum Powder	1 1/2 oz.
Sodium Silicate	2 1/2 oz.
Casein	2 1/2 oz.

Glaze for Wood or Metal

Casein	100 lb.
Borax	7-15 lb.
Trisodium Phosphate	7-15 lb.
Hexamethylenetetramine	0.8 lb.
Castor Oil	1-5 oz.
Clovel	1 oz.

Window Shade Sizing

Casein	10 lb.
Borax	8 lb.
Animal Glue	26 lb.
Paraformaldehyde	1 oz.
Water	50-100 gal.

Dissolve above and then add with vigorous stirring.

Sash Cord Impregnant

Lactic Casein	10 oz.
Borax	2 oz.
Pigment	60 oz.

Soap Solution	4 oz.
Caustic Soda	0.5 oz.
Ammonium Sulphate	0.8 oz.
Water	remainder

The soap solution can be sodium resinate or the potassium salt formed by boiling potassium carbonate (1 part) with carnauba wax (15 parts). The ammonium sulphate is added after all the other ingredients are in solution. The pigment could be china clay or talc colored to shade with a brown lake. The composition given would require further adjustment with water to give the right consistency in the coating tank.

Manufacture of Casein

"Rennet Casein" suitable for making Galalith and similar plastics is best obtained as follows: To fresh skim milk at 35° C. add sufficient rennet to effect coagulation in 15-20 minutes; stir 5-10 minutes and warm to 65° C. at the rate of 1° per minute; decant twice with water at 25°; drain and press out as much water as possible, disintegrate the press cake and dry at 43-45°C.

Codling Moth Tree Band

Water	2 gal.
Ammonia	2.4 fl. oz.
Casein	4 oz.
Mineral Oil Refined (65-75 sec.)	8 gal.

Paper Coatings
Casein Glue

Casein	100 lb.
Water	50 gal.
Borax	17 lb.
Ammonia 26°	1 qt.

The casein is preferably soaked a few hours in the water, the borax dissolved in a little hot water-added, and the whole cooked to 160° F. till no undissolved particles of casein remain. Then the ammonia is added and the glue cooled.

Wax Emulsion

Carnauba Wax	50 lb.
Water	50 gal.
Soap	12 lb.

The soap is dissolved in the water and brought to boiling. The wax is added and boiling continued until all is emulsified. The emulsion is preferably stirred continuously until cold. The soap may be any good grade of washing soap free from rosin.

Yellow

Clay	50 lb.
Blanc Fixe Pulp (70% dry)	50 lb.
Chrome Yellow Pulp (50% dry)	125 lb.
Talc	12 lb.
Casein Glue	11 gal.
Carnauba Wax Emulsion	4 gal.

Blue

Prussian Blue Pulp (30% dry)	100 lb.
Violet Lake Pulp (35% dry)	75 lb.
Maroon Lake Pulp (35% dry)	75 lb.
Casein Glue	8 gal.
Carnauba Wax Emulsion	3 gal.
Talc	4 lb.

Pearl

Clay	50 lb.	Pulped together
Blanc Fixe Pulp	50 lb.	
Italian Talc	4 lb.	
Ultramarine Blue	5 lb.	
Water	4 gal.	
Casein Glue		12 gal.
Carnauba Wax Emulsion		4 gal.

Red

Red Pulp (40% dry)	200 lb.
Talc Italian	4 lb.
Casein Glue	12 gal.
Carnauba Wax Emulsion	6 gal.

Paper Coating -- Friction Finish --

Yellow

Casein	200 lb.
Borax	12 lb.
Ammonia	5 qt.
Water to make	150 gal.

Water	43 gal.
Talc	23 lb.
Clay	200 lb.
Blanc Fixe Pulp	390 lb.
Medium Yellow Pulp	18 lb.
Carnauba Wax Emulsion	16 gal.
Casein as above	32 gal.

Paper Coating -- White -- Soft Sized

Water	165 gal.
Clay	1300 lb.

Stir 15 min. in a rapid dissolver and add

Dry Casein	140 lb.
Stir 15 min. and add	
Dry Borax	18 lb.
Stir 5 min. and add	
Ammonia	4 qt.

Heat to 140° F. and stir till casein is dissolved and cool to room temp. -

Strain before using.

If hard sized coating is desired, increase the amount of casein until the desired degree of sizing is obtained.

Paper Coating
(Dull Black Velvet Finish)

Casein Solution (25-30% Casein)	100
Ivo Bone Black	75

Grind mixture in a suitable mill and use same day if no preservative is added.

Paris Paste, a colloidally dispersed carbon black can be used to give an intense black color. This has already been finely ground and goes into aqueous media readily.

Paper Coating

The following formula gives a solution which does not readily gel:

Lactic Casein	5.75%
Caustic Soda	.25%
Sodium Bicarbonate	.5 %
Blanc Fixe	33 %
Satin White	33 %
Water	27.5 %

The sodium bicarbonate should be added after solution of the casein by the caustic.

Clay works particularly well with casein solutions giving a smooth adherent film only a little less glossy than that given by satin white.

Blanc fixe and precipitated chalk are used for matt or semi-matt finishes. Neither clay nor blanc fixe gives such a waterproof coating as satin white. Depending on the effect desired and the nature of the casein and the fineness of grinding of the pigment, one part of casein will bind satisfactorily about 20 parts of barytes, 15 parts of chalk, 15 parts of coarse clay, 12 parts of fine clay, and 10 parts of satin white. In general, the greater the amount of mineral matter present the greater the gloss and the more readily does the paper receive the ink.

Paper Coating
Formula No. 1

Argentine or Silver Paper:

Argentine Pulp 40%	90	lb.
Casein Solution (1/4 lb. per gal.)	2 1/2	gal.
Carnauba Wax Emulsion	1/2	gal.
Tuluol	1	pt.
Carbon Tetrachloride	1	pt
Nigrosin	9	oz.

The casein solution is made as follows:

Casein	62	lb.
Borax	7	lb.
Trisodium Phosphate	7	lb.
Water to make	50	gal.

The carnauba wax emulsion is made with this formula:

Carnauba Wax	140	lb.
Castile Soap	20	lb.
Water to make	140	gal.

No. 2

A coating mixture which will give a high finish when calendered is made up as follows:

Water	65	gal.
Soda Ash	3	lb.
Ammonia	4	gills
Satin White Pulp	440	lb.
English Clay	650	lb.

Stir until thoroughly mixed and smooth and add the following casein solution:

Water	50	gal.
Casein	100	gal.
Soda Ash	10	lb.
Trisodium Phosphate	7	lb.
Borax	5	lb.
Ammonia	6	gills

This coating mixture will produce a high finish when calendered, that is suitable for the highest grade lithographic or process printing.

Paper Coating Composition

A typical formula is as follows:

Lactic Casein	9%
Borax	2%
Blanc Fixe	60%
Talc	1%
Special Soap Solution	4%
Water	24%

The soap solution is made by boiling together

Carnauba Wax	20.0 %
Potassium Carbonate	1.25%
Water	72.75%

A greater degree of water resistance can be secured by substituting for the borax one-sixth of its weight of caustic soda, and when solution is complete adding ammonium sulphate to the extent of one and one-half times the weight of caustic soda employed. All the additions are naturally made as solutions.

The most widely practised method of making up the finished coating solution consists, broadly, in first dissolving the casein in the manner stated above, reducing the temperature to 80-100° F. and adding it to a perfectly smooth thin slip of the mineral fillers and water. Any other components, such as foam reducers, are then added, and the batch taken to the coating machine.

Transfer Printing Paper
U. S. Patent 1,965,257

Rubber Latex (60%)	40 lb.
Casein	10 lb.
Zinc Stearate	5 lb.
Paraffine Emulsion	50-100 lb.
Formaldehyde (40%)	5 lb.
Triethanolamine	2 lb.
Water	2 lb.

Tarpaulin or Tent Waterproofing
Australian Patent 17,598

Rubber Latex	1-2 lb.
Linseed Oil	1/2 lb.
Casein	2 lb.
Water	16 gal.

Coating for Rubber Goods
British Patent 427,228

Latex	100 lb.
Glue	1-5 lb.
Barytes	100 lb.
Titanium Dioxide	50 lb.
Rosin Oil	10 lb.
Casein	5-20 lb.
Sulphonated Castor Oil	5 lb.
Ammonia (28%)	8 lb.
Formaldehyde	10 lb.
Color	to suit

Water sufficient to give a final concentration of total solids of 45-50%.

Aqueous Latex Dispersions for Artificial Leather

A mixture composed of "smoked sheets" (rubber) 100, gasoline 200, oleic acid 8, 25% ammonium hydroxide solution 20, casein 20, sulphur 8, zinc oxide 10, "Kaptex" 2, thiuram 1 part and water in accordance with requirements, produces stable emulsions when diluted with up to 50 volumes of water.

Non-Adhesive Mold Liner

To a mixture of casein 45, glycerol 45, and kaolin 10 parts, add water to the required consistency. Apply 2-3 times on both sides of the cotton material. Dry 1-1½ hours. Then treat with formaldehyde. The total time is 6-7 hours.

Anti-Foaming Agent: For casein, etc. The addition of as little as 1/10% of diglycol laurate serves to break the foam on skim milk or whey. The best results are obtained when the diglycol laurate is added to the whey at some point between the pump and the receiving vat. In the manufacture of low-foaming acid precipitated casein, diglycol laurate is not strained off with the whey nor does it volatilize under the conditions of drying the casein.

Mineral Oil Emulsion

Casein	6 lb.
Water	60 lb.
Mineral Oil	50 lb.
Red Oil (Oleic Acid)	4 lb.

In using casein it should be strewn in the surface of the water which is being stirred with a high speed agitator. The oil or other water in soluble material is then run in slowly while stirring. The pigments or abrasives are then added in the same way.

Polish, Emulsion

Casein	3 lb.
Water	17 lb.

Allow to soak for 15 minutes; stir until all particles are gone. Put into a mayonnaise type of mixer and, while beating add to it slowly

Mineral Oil	80 lb.

The above gives a white heavy cream which may be diluted with water to give a milky liquid.

Shoe Cream, Neutral

Carnauba Wax Emulsion	50

Heat to 200° F. and to it add following solution warmed to 150° F. and stir until smooth.

Turpentine	29
Water	24
Casein	3
Soap Flakes	1

White Shoe Cleaner, Paste
(For use in tubes)

Soap Flakes	10
Casein	5
Water	35
White Pigment	150
Preservative to suit	

Cellular or Light Weight Concrete
U. S. Patent 1,985,905

A slurry is formed by mixing cement with following foam producing compound:

Water	500 lb.
Casein	100 lb.
Slaked Lime	25 lb.
Benzaldehyde	7 lb.
Beta Naphthol	1 lb.
Arsenic Trioxide	1 lb.

INDEX

Acetaldehyde 34
Acid Casein Binder 79
Acidity Test 22
Adhesive Paste 57
Adhesive Power 25
Adhesives 27-31-32-34
35-38-49-50-51-52-54-57-58
Adhesives, Testing 43
Albumen 2
Alkali Casein Ratios 29
Alkalinity Working
Life Ratio 37
Ammonium Sulphocyanate 57
Analytical Constants
of Casein 19
Anti-foaming Agent 94
Applying Glue 43
Ash Content 7

Binder, Emulsion 74-75
Blood Albumen Casein
Glue 52
Borax Casein 32
Borax Casein Solutions 6
Brominated Casein 16
Brushability, Improving 63

Carbon Dioxide 62
Casein Alkali Ratios 29
Casein, Composition of 8
Casein, "Dissolving" 65
Casein Flow-sheet 4
Casein Hot-Air Drier 12
Casein, Making Pure 3
Casein Mesh Standards 18
Casein Oil Binder 80
Casein Production 2-9
Casein, Solubility 28-29
Casein "Solvents" 32
Casein Specifications 6
Casein Textile Fibre 85
Casein Xanthogenate 16
Chromium Peroxide 34
Chromium Potassium
Sulphate 34
Citric Acid 2
Cleaner, White Shoe 95
Cold Glue 42-50
Colored Casein Paint 80
Colored Paper Coatings 88
Colors 63
Colostrum 2
Concrete, Light Weight 95
Cork Compositions 84
Cork Liner Adhesive 57
Corrosive Sublimate 64
Covering Power 64

Defoaming 94
Degumming Fibers 85
Dissolving Casein 32-65
Drier for Casein 15-16
Driers 65
Dry Joint Strength 46
Drying Casein 3
Dusting, Preventing 41

Emulsion Binder 74-75
Emulsion Paint 70
Emulsions, Oil 65
English Casein Paint 74-78
Ethanolamines 57

Fat, Milk 2
Fat Test 21
Fehling Solutions 23-24
Fillers 63
Flow, Improving 65
Foam Killer 94
Formaldehyde 34-64
French Casein Paint 74
Furfurol 34
Furniture Glue 50

Galalith 83
Galalith to Metal
Cement 58

Glaze 86
Globulin 2
Gloss, Improving 61
Gloss Paint 61
Glue Liquifiers 55
Glue Mixers 42
Glue Paint Binder 80
Glue, Prepared 31
Glue, Wet-mix 31
Glycerine 39
Grades of Casein 17
Ground Casein 17
Gyro Dissolver 62-66

Hard-wood, Synthetic 84
Hardening Casein Coatings 83
Hexamethylenetetramine 64
Hydrochloric Casein Process 4

Insect Bands for Trees 87
Insolubilizing Casein 34-64
Ivory Substitute 85

Label Glue 58
Lacquer, Casein 68
Lactic Acid Casein 17
Lactose 2
Lactose Test 23
Lanital 85
Latex 65
Leather, Artificial 93
Leather Finish 85-86
Lime Hydrate 61
Lime Hydrate - Casein Ratio 62
Lime Paints 61
Lipoids 1
Low Foaming Glue 50
Lowering Viscosity of Casein 7
Lumping 41

Metallo-Caseinates 34
Milk, Composition of 1
Mineral Oil Emulsion 94
Mold Growth, Preventing 64
Mold Liner, Non-adhesive 93

Nitro Casein 16
Non-peeling Coatings 64

Oil Coated Casein 41
Oil Casein Paints 65
Oil Emulsions 65

Paint Binders 61
Paint, Dull Finish 67
Paint, Powdered 67
Paints 60-63-65-67 68-69-70-71-73-74-75-80-81
Paper Bag Adhesive 58
Paper Coatings 82-83-87-88 89-90-91-92
Paper Coating Casein Binder 81
Para Casein 8
pH Values 28
Phenol Formaldehyde Resin, Making 71
Phenolic Resins 65
Phenols 61
Pigments 63
Pine Oil 65
Pine Oil Emulsion 71
Plastic Wood Dough 57
Plywood Adhesive Spreader 30
Plywood Glue 49
Plywood Shear Test 43
Polish Emulsion 94
Polish, Shoe 94
Precipitation of Casein 3
Preservatives 49
Printing Ink Binder 80
Printing Roller 85
Protein 1-21

INDEX

Putty 59

Radiator "Stop-leak" 86
Rennet Casein 6-8
Rennet Casein, Manufacture of 87
Resin Emulsion Paint 71
Retarding Thickening 34
Rubber Goods Finish 93

Sash Cord Impregnant 86
Self Souring Process 4
Settling, Preventing 68
Settling, Retarding 63
Shear Resistance Test 47
Shoe Cream 94
Siccatives 65
Sign Paints 68
Silicofluorides 40
Sizing, Window-shade 86
Skim Milk 2
Sodium Arsenate Casein 32
Sodium Carbonate Casein 32
Sodium Fluoride 40
Sodium Fluoride Casein 32
Sodium Metasilicate 73
Sodium Phosphate Casein 32
Sodium Silicate 37-38
Sodium Stannate Casein 32
Soy Bean Glue 53-54
Specific Rotation 25
Spinning Spool Paint 70
Stability 43
Starch Test 21
Storing Casein 19
Strength of Joints 43
Sulphuric Process Casein 5

Tannic Acid 34
Tarpaulin Waterproofing 93
Testing Casein 17-18-19 20-44-45
Testing Casein Paint 67
Thiourea Glue 55
Tin Can Paint 70
Tin Glue 58
Trade Brands 61
Traffic Line Paint 81
Transfer Printing Paper 92
Trisodium Phosphate 40
Turbomixers 72
Turkey Red Oil 64

Urea Casein Glue 55
U.S. Cold Water Paint Specifications 74

Vacuum Drying Oven 14
Vegetable Proteins 53
Veneer Glue 51
Viscosity, Altering 29
Viscosity Change with pH 33
Viscosity Test 24

Wall Paint 63
Washing Casein 3
Water-paints 60
Waterproofing Casein Coatings 83
Waterproofing Glues 54
Waterproofing Tents 93
Water Resistance, Improving 64
Water Resistance, Increasing 68
Water Resistance Test 47
Water-resistant Paints 60
Wax Emulsion 87
White Casein Paint 80
White Shoe Dressing 95
Wood Lacquer, Casein 68
Working Life 32

USEFUL BOOKS

The Chemist's Yearbook 1275 pages	F.W.Atack 1938	$6.00
The Soybean Industry 221 pages	A.A.Horvath 1938	$4.00
Principles of Organic Chemistry 664 pages	H.P.Starck 1938	$5.00
Handbook of Food Manufacture 1938	F.Fiene & S.Bluementhal	$6.00
Modern Rubber Chemistry 342 pages	H.Barron 1938	$7.50
Fluorescence and Phosphorescence 1938	E.Hirschlaff	$1.50
Utilization of Fats 1938	H.K.Dean	$6.00
General Science 1938	J.C.Platt	$1.50
Shoe Creams and Polishing Waxes 1938	Davidson and Davidsohn	$4.00
The Technology of Solvents 1938	O.Jordan	$10.00
Applied Mycology and Bacteriology 1938	Galloway and Burgess	$4.00
A Concise Pharmacology 1938	Hobart and Melton	$3.00
The Standardization of Volumetric Solutions 1938	R.B.Bradstreet	$3.00
Steels for the User 280 pages	R.T.Rolfe 1938	$8.50

Metal Coloring, Plating and Finishing H.Krause
1938 $5.00

Nematodes Parasitic in Animals G.Lapage
172 pages 1938 $1.75

Animal Life in Fresh Water H.Mellanby
1938 $3.50

Microchemical Methods, A Course in C.I.Wilson
1938 $3.00

Dipole Moments J.W.LeFevre
1938 $1.50

Wetting and Detergency W.Clayton
207 pages 1937 $6.00

Modern Glass Working and Laboratory Technique M.C.Nokes
153 pages 1937 $3.00

Biological Laboratory Technique J.B.Gatenby
127 pages 1937 $3.00

Field Tests for Minerals E.H.Davison
60 pages 1937 $3.00

Physical Chemistry J.N.Bronsted
394 pages 1937 $5.00

Ebulliometry
(The Physical Chemistry of Distillation) W.Swietoslawki
204 pages 1937 $3.00

Sterols and Related Compounds E. Friedman
100 pages 1937 $3.00

Basic German for Science Students M.L.Barker
186 pages - 3rd ed. 1937 $2.50

A Scheme of Inorganic Qualitative Analysis E.M.Stoddart
1937 $1.00

Properties of Matter D.N.Shorthose
168 pages - 2nd ed. 1937 $2.00

The Catalytic Action of Surfaces 101 pages	J.E.Nyrop 1937	$3.00
Light 328 pages	V.T.Saunders 1937	$2.50
Chemical Calculations 95 pages	C.M.Jones 1937	$1.25
Volumetric Analysis 233 pages	A.J.Mee 1937	$3.50
Canning Practise and Control 254 pages	Jones and Jones 1937	$10.00
Metal Plate Work 539 pages	C.J.Millis 1937 - 2 vols.	set $4.80
Cosmetic Formulary 279 pages	H.Bennett 1937	$3.75
More for Your Money 251 pages	H.Bennett 1937	$2.75
Technology of Plastics 206 pages	H.W.Rowell 1936	$4.00
Inorganic Chemistry 462 pages	G.Morgan F.Burstall 1936	$6.00
Pocket Book for Chemists 460 pages	T.Bayley 1938	$2.00
Leather Chemists' Pocket Book 394 pages	H.R.Proctor 1936	$6.00
Boiler Feed Water Treatment 256 pages	F.J.Matthews 1936	$5.00
The Making and Molding of Plastics 238 pages	L.M.T.Bell 1936	$5.00
The Principles of Leather Manufacture 688 pages	H.R.Proctor 1936	$8.50
Technical Aspects of Emulsions 150 pages	1936	$4.00

Chemical Formulary	H.Bennett	
Vol. 1 1933	604pp	$6.00
Vol. 2 1934	570pp.	$6.00
Vol. 3 1936	566pp	$6.00
Vol. 4	In preparation	$6.00
An ABC of Plasticisers		
1936		$1.25
The Chrome Tanning Process	E.W.Merry	
143 pages	1936	$4.50
The Chemistry of Rubber	H.Freundlich	$1.25
1936		
Distillation	J.Reilly	
120 pages	1936	$1.25
Laundry Chemistry	A.Harvey	
118 pages	1935	$1.75
Engineers' Sketch Book of Mechanical Movements	T.W.Barber	
355 pages - 3000 illus.	1934	$4.25
Modern Shoe Dressing	W.D.John	
153 pages	1934	$5.00
Shoe Finishers Guide	W.D.John	
130 pages	1934	$5.00
Drying Oils and Dryers		
90 pages	1934	$1.25
Workshop Receipts		
Volumes I,II,III,IV,	1926-1932	ea. vol. $2.50
and supplement		set $10.00
Cements, Pastes, Glues, Gums	H.C.Standage	
164 pages	1931	$1.50
Spectroscopy in Science and Industry	S.J.Lewis	
Fully illustrated		$1.50
Practical Microscopy	Martin and Johnson	
116 pages - Fully illustrated		$1.50

Practical Organic Chemistry — Sudborough and James
330 pages - Fully illustrated — $3.25

Plant Diseases — W.F.Bruck
152 pages — $1.00

Production and Treatment of Vegetable Oils — T.W.Chalmers
152 pages — $8.50

Insulin — Hill Howitt
240 pages — $5.00

Principles and Practice of Lubrication — Nash and Bowen
356 pages — $7.25

Portrait Photography — H.Williams
Illustrated with 32 half-tone plates and 67 figures — $4.25

HEADQUARTERS

FOR

PRESERVATIVES

TACKIFIERS

EMULSIFYING AGENTS

WETTING AGENTS

FLEXIBILIZERS

DEFOAMERS

FOR

CASEIN

SHELLAC

ADHESIVES

ETC.

SEND FOR
OUR LATEST CATALOGUE
FREE ON REQUEST

GLYCO PRODUCTS CO., Inc.

148 LAFAYETTE STREET (Dept. C) NEW YORK, N. Y., U. S. A.

Date Due

JUL 27 '60			
OCT 2 8 1974	OCT 1 8 1974		
JUN 2 2 1981			
NOV 2 3 1981	DEC 1 1 1985		

Library Bureau Cat. No. 1137

Casein and its uses; sci
388 H128c
3 1262 03157 0822

388
H128c
AGRI-
CULTURAL
LIBRARY
18534